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THE CHEMISTRY OF PETROLEUM DERIVATIVES

BY

CARLETON ELLIS

INDUSTRIAL RESEARCH CHEMIST

VOLUME I

BOOK DEPARTMENT
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Preface

For more than a decade some chemists interested in petroleum technology have maintained that the numerous hydrocarbons abundantly available in the product of our oil wells will ultimately provide the basis of a new organic chemical industry yielding new substances in as great variety and of as essential utility to civilization as the products of coal tar. The realization of this dream has been hindered by the extraordinary difficulties of separating chemical individuals in a satisfactory state of purity from the complex mixture which constitutes the mother substance, but in spite of the uncertainties of working with partially purified raw materials a vast amount of information has been accumulated on the behavior of individual hydrocarbons derived from petroleum.

Interest in the chemical utilization of aliphatic hydrocarbons has been greatly stimulated within the last few years by the development of more efficient methods of fractional distillation for separating the lower-boiling constituents of petroleum and of fractional solution in a variety of solvents for isolating higher-boiling compounds. Progress toward the quantity preparation of pure compounds has been rapid and the literature bearing upon their elaboration has become voluminous. During the past few years the amount of material on the subject has increased several fold and the number of investigators studying problems related to it has grown enormously.

In this situation the difficulties faced by the individual research worker in collecting and collating the widely diffused literature bearing upon his problem have become well-nigh insurmountable. Such a task has been in progress in the author's laboratory for some years and so great was the mass of material accumulated and the labor involved in making it usable that the decision was reached to publish the result in order to place it at the disposal of the many others interested. That is the reason for the present volume. Every effort has been made to make it complete and to include in it references to all published material of both purely scientific and industrial interest as well as to the vast amount of information contained in patents on the subject.

In the preparation of the manuscript many collaborators have co-operated and the author takes this opportunity to extend his thanks to them. Prof. Julius von Braun, Prof. J. R. Bailey, Prof. H. B. Haas, Dr. D. A. Howes, Dr. Ernest B. Kester, Prof. Donald B. Keyes, Mr. W. B. Plummer, and Dr. Sherlock Swann, Jr., have materially assisted in the preparation of certain chapters. The members of the research and technical departments of the Standard Oil Company of New Jersey have given valuable constructive criticism of many parts of the volume. I wish especially to express my appreciation to Dr. H. M. Stanley and to Mr. D. H. Killeffer; to Dr. Thomas C. Whitner, Jr., Mr. Ferdinand F. E. Kopecky, and other members of my laboratory staff; and to Dr. Frank B. Root and the Ellis-Foster Company for their contributions to this huge task.

C. E.

Ellis Laboratories,
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Introduction

World production of petroleum is approaching a quarter of a billion tons annually but, with new deposits constantly being found—indicative of the widespread distribution of oil throughout the land and under the sea—the apprehensions of a decade ago that the supply of this essential raw material would soon be exhausted no longer obtain. The replacement of such fears by the assurance of tremendous supplies for a long period to come of this important commodity should have given an impetus to pure chemical research in the domain of petroleum commensurate with the vastness of the deposits.

This, however, appears not to have been the case. Despite the great number of chemists, physicists, engineers and other technically trained men engaged in the study and handling of petroleum, very little is known thus far of its actual chemical make-up.

In certain other important chemical industries originating by virtue of a supply of particular substances, comprehensive research of a scientific character preceded the commercial development of the field. Of these, the coal-tar industry stands foremost. So provocative of industrial recognition have been the results of scientific study of coal-tar hydrocarbons that the layman frequently asks why the petroleum chemist does not direct his skill similarly to the chemical utilization of the hydrocarbons of crude oil.

There exists, however, a significant difference between the two groups of hydrocarbons from coal tar and from crude petroleum in that the former (at least so far as the lower and intermediate members are concerned) are easily separated one from another, which permits the properties of the chemically individual hydrocarbons to be ascertained with comparative ease. As a result of such studies of the pure substances, commercial products have become available for treatment and conversion by well-understood industrial methods. The group of terpene hydrocarbons has been similarly well elucidated in the hands of chemists.

Why, then, is so little known chemically about a commodity of such import as petroleum? The following explanation is offered.

Unlike the reactive terpene hydrocarbons and most of those present in coal tar, the hydrocarbons of petroleum oil are, in the main, comparatively indifferent to the majority of the usual conversion reagents. This observation coupled with the recognition of the possible existence of an extraordinary number of hydrocarbon individuals in crude oil and its distillates has impelled many chemists to view with dismay the prospect of founding an extensive chemical industry on petroleum. Hence for the most part they rest content to continue their efforts mainly in the direction of the treatment of crude oil by refining procedures which, although often displaying chemical talent and ingenuity of high order, perforce are conducted largely on an empirical plane. Still others look for some explorer to rise from the ranks with banners flying and lead them from this empiricism along a course as definite, informative and expansive as that so well charted in the chemistry of coal-tar oils.

No such leader has yet appeared. Here and there a man of science resolves some small part of the disorder. Witness, for example, the work of Julius von Braun on naphthenic acids and the researches of J. R. Bailey on the nitrogen compounds of petroleum.

A group of pessimists, by no means small in number, is not lacking to hold out a warning hand of futility to these progressives and to call attention to those calculations which show that a paraffinic hydrocarbon of, say, nine carbon atoms could be represented by 35 isomers (55, if stereoisomers are included) and that one of 20 carbon atoms would have 366,319 possible isomers, a number swollen by including stereoisomers to the enormous figure of 3,395,964!

That petroleum contains a multiplicity of isomers is a common observation. That all isomers theoretically possible are to be found therein is by no means probable. In fact experimental work has already demonstrated that of a family of isomers found in a petroleum distillate some one member usually predominates.

A further obstacle to rational chemical development has been the pronounced variation between crude petroleums from different parts of the world. Those from the Pennsylvania oil regions, for example, are commonly considered highly paraffinic, those from California include large percentages of aromatic compounds, and those from Russia and Galicia contain substantial proportions of hydroaromatics. Methods, therefore, which will allow the identification of certain types of hydrocarbons in one crude petroleum may not be applicable to another in which entirely different hydrocarbons predominate. This variation in composition adds to the confusion with respect to the presence of individual hydrocarbons.

Despite the foregoing, observers note a slow but steady advance in the chemistry of petroleum both technologically and scientifically. Technology has, perhaps, shown greater progress than strictly scientific knowledge. Thus, the urgent need for toluene during the World War resulted in the development of cracking processes which yielded that hydrocarbon in significant quantities just as other commercial needs have produced other developments.

At about the same time the experimental work conducted by the author supplied the oil industry with methods for the conversion of olefins from cracked products into secondary alcohols. From these by catalytic oxidation or dehydrogenation various ketones became available. Numerous esters prepared from the alcohols found favor in the lacquer industry and elsewhere.

This enterprise established in one of the refineries of the Standard Oil Company of New Jersey probably represents the first permanent industrial plant for making chemical derivatives, other than hydrocarbons, from petroleum.

Later work by others has resulted in the commercial production of glycols and their ether derivatives, well received by the coating industry.

The pages following embrace as comprehensive a review of the chemical derivatives of petroleum as publication limitations permit. That there have been many disappointments in the laboratories of petroleum chemists when the hope of synthesis of industrially important compounds from petroleum has failed is to be expected. The surprising fact is that results of such far-reaching importance in petroleum chemistry already have been attained.

In a comprehensive work of this kind, including as it does mention of the conclusions of a vast number of investigators, an appraisal of the merits and demerits of all the proposals offered manifestly is impossible. The author, therefore, has had to content himself for the most part merely with a brief statement of the findings of and the conclusions drawn by the investigators enumerated

CHEMISTRY OF PETROLEUM DERIVATIVES

Chapter 1

Chemical Nature of Petroleum and Natural Gas. Pure Hydrocarbons from Petroleum

Crude petroleum as it issues from wells consists mainly of a mixture of hydrocarbons of many chemical types and of varying degrees of molecular complexity. Besides hydrocarbons, smaller proportions of compounds of oxygen, nitrogen, and sulphur are often present together with mechanically held gas, water, clay, and inorganic substances in solution or colloidal suspension. Petroleums from different localities, and even from dissimilar oil sands in the same field, often exhibit great variations in appearance, chemical composition and properties.[1] For example, the crude oil of the Kettleman Hills field, California, frequently consists almost entirely of comparatively volatile hydrocarbons and has been marketed as a motor fuel directly without distillation or refining.[2] On the other extreme, the black asphaltic and highly sulphurous Mexican crudes often contain no gasoline fractions whatever. Petroleums differ not only in their content of impurities (such as sulphur compounds) but also in the chemical type and average molecular complexity of the hydrocarbons present, which may range from the simplest gaseous members of the paraffin series to hydrocarbons of molecular weight exceeding 1000.[3] Besides the paraffin and cycloparaffin (naphthene) hydrocarbons, benzenoid hydrocarbons as well as more complex polynuclear aromatic and cycloparaffin hydrocarbons also occur in crude petroleum.

The existence of unsaturated hydrocarbons in crude petroleum, prior to distillation, is a question which has aroused considerable controversy. Certain unsaturated hydrocarbons and terpene-like substances have been reported by Zaloziecki[4] and LeBel,[5] and Markownikow and Oglobin[6] obtained evidence of the presence of hydrocarbons of the acetylene series. Most of the work on this subject has been carried out on distillates, i.e., fractions obtained on subjecting the crude oil to distillation, so that these unsaturated products may have been formed by pyrolysis.[7] When distillation is carried out at low temperatures and pressures, the proportion of unsaturated substances in the gasoline and kerosene fractions is usually exceedingly small.[8] Most of the published analytical figures for gasoline and kerosene fractions of various crudes show the presence of relatively small amounts of unsaturated hydrocarbons.[9] Though the complete absence of unsaturated hydrocarbons (of the gasoline and kerosene range) from *crude* petroleums cannot be presumed on the evidence available, it appears that the proportions of such hydrocarbons, if they are present at all, are usually quite small.

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[1] These differences are pointed out by Egloff, *J. Chem. Education,* 1933, 10, 524.

[2] Robertson, *Ind. Eng. Chem.*, 1930, 22, 1268.

[3] Mabery (*Ind. Eng. Chem.*, 1923, 15, 1233) mentions a fraction having a formula $C_{125}H_{231}$ with a molecular weight of 1730.

[4] *Ber.*, 1894, 27, 2081; *Chem. Soc. Abs.*, 1894, 66 (1), 611; *Dinglers Polytech. J.*, 1894, 75, 114; *Chem. Zentr.*, 1894, 2, 530.

[5] *Compt. rend.*, 1872, 75, 267; *Chem. Soc. Abs.*, 1872, 25, 886; *Compt. rend.*, 1875, 81, 967; *Chem. Soc. Abs.*, 1876, 29, 539.

[6] *J. Russ. Phys. Chem. Soc.*, 1881, 13, 179; *ibid.*, 1882, 14, 36; *ibid.*, 1883, 15, 237; *Chem. Soc. Abs.*, 1882, 42, 390; *ibid.*, 1884, 46, 1276; *Bull. soc. chim.*, 1884, 41, 258.

[7] See, for example, Tausz and Wolf, *Z. angew. Chem.*, 1919, 32 (1), 317; *Chem. Abs.*, 1920, 14, 621.

[8] See, for example, Lachowicz, *Ann.*, 1883, 220, 188; *Chem. Soc. Abs.*, 1884, 46, 166.

[9] A bibliography of chemical analyses of petroleums is given in Redwood, "A Treatise on Petroleum," Charles Griffin and Co., Ltd., London, 1913, 1, 237-267.

NATURAL GAS

The simpler hydrocarbons of the paraffin series are normally gaseous and occur in enormous quantities in the so-called natural gas which frequently accompanies crude petroleum. Natural gases, which may be regarded as gaseous petroleums, also exhibit great variations in chemical composition, but for the most part, they consist of lower paraffins: methane, ethane, propane, with smaller quantities of butane, pentane, and other hydrocarbons up to octane, together with smaller proportions of nitrogen, carbon dioxide, hydrogen sulphide, and, in a few cases, the rare gas helium.[10] Small proportions of the vapors of benzenoid and cycloparaffin hydrocarbons (naphthenes) are also undoubtedly present in some gases which are in contact with aromatic or highly naphthenic crudes. Thus, Erskine[11] found that a sample of Pennsylvania natural-gas gasoline, recovered by absorption, contained 0.6 per cent of benzene, 0.6 per cent of toluene and 1.2 per cent of m-xylene. The presence of cyclopropane and cyclobutane in natural gases has been suspected though not definitely proved.[12] On the other hand, gases such as olefin or acetylene hydrocarbons, carbon monoxide and hydrogen, which are characteristic products of pyrolytic reactions, have never been found in natural gas.

Natural gases are roughly divided into two classes, "dry" and "wet" gases. High-pressure gas from new fields or gas not associated with crude petroleum, and containing only relatively small amounts of the higher gaseous paraffins, is called dry gas, whereas low-pressure gas associated with petroleum, and containing relatively large amounts of easily liquefiable hydrocarbons, is termed wet gas. Although the majority of gas wells do not yield oil, gas invariably accompanies oil in the strata. Dry gases consist mainly of methane with varying amounts of nitrogen and carbon dioxide. In illustration of the great variation in composition of gases from different localities, it may be noted that Botolfsen[13] described one containing very large proportions of nitrogen and a Mexican natural gas, consisting of almost pure carbon dioxide, has been exploited as a source of "dry ice" (solid carbon dioxide).[14]

Natural gas occurs in parts of the world where petroleum is found—in Russia, Rumania, Poland, Burma, Persia, Mexico, South America, Canada, and more especially in the United States. It also probably occurs in the atmospheres of the large planets, lines due to methane molecules having been identified in the spectra.[15] Practically 98 per cent of the world's commercial production of natural gas is accounted for by the United States. Although over half the states of the

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[10] The occurrence of helium in natural gas is discussed by von Angerer and Funk, *Z. physik. Chem.*, 1933, **B20**, 368; *Chem. Abs.*, 1933, **27**, 2877; Levi, Nasini and de Cori, *Gazz. chim. ital.*, 1932, **62**, 799; *Chem. Abs.*, 1933, **27**, 686; Krejci-Graf, *Petroleum Z.*, 1932, **28** (14), 12; *Chem. Abs.*, 1932, **26**, 4567. The helium industry is reviewed by Kvasha, *Prirodnuie Gazui*, 1931, **2**, 156; *Chem. Abs.*, 1932, **26**, 1717; Rosewarne and Offord, *Canadian Dept. Mines, Mines Branch Rept.* 727, 1932, 42; *Chem. Abs.*, 1933, **27**, 3296. The extraction of helium from gas mixtures is described by Bottoms, U. S. Patent 1,850,529, Mar. 22, 1932; *Brit. Chem. Abs.* **B**, 1933, 227; U. S. Patents 1,881,115 and 1,881,116, Oct. 4, 1932; *Brit. Chem. Abs.* **B**, 1933, 704; patents assigned to Helium Co.; Cherepennikov, Russian Patent 25,598, 1932; *Chem. Abs.*, 1932, **26**, 5391.

[11] *Ind. Eng. Chem.*, 1926, **18**, 722.

[12] See Brooks, *Ind. Eng. Chem.*, 1924, **16**, 185; Burrell, *ibid.*, 1928, **20**, 602.

[13] *Arch. Math. Naturvidenskab*, **40**, Pts. I and II; *Chem. Abs.*, 1932, **26**, 281. Botolfsen also described a natural gas consisting of practically pure methane.

[14] Martin, *Ind. Eng. Chem.*, 1931, **23**, 256; see Chapter 7. Recovery of carbon dioxide from natural gas by absorption in triethanolamine has been described by Albright [*Refiner and Natural Gasoline Mfr.*, 1932, **11** (1), 19; *Chem. Abs.*, 1932, **26**, 3090; see also Chapter 23].

[15] Wildt, *Naturwiss.*, 1932, **20**, 851; *Brit. Chem. Abs.* **A**, 1933, 6.

United States produce some natural gas, the principal fields are located in Oklahoma, Texas, California, Louisiana, West Virginia, and Pennsylvania. The production of this gas in the United States in 1928 was in the neighborhood of 1,568,139,000,000 cubic feet.[16]

In chemical composition, natural gases from different localities exhibit wide variations, as may be seen from the following tables. It is desirable at this stage to point out that many of the older, and even some of the more recent, analyses are untrustworthy on account of the inadequacy of the analytical methods employed. In the older methods of analysis, for example, no differentiation was made between the various homologous paraffins, the total hydrocarbon content being usually recorded simply as methane. The development of low-temperature fractionation methods of analysis has rendered possible a fairly accurate differentiation and estimation of the individual hydrocarbons present.[17]

Table 1 contains analytical figures for various natural gases in the United States.[18] Though no differentiation is made betweeen the individual gaseous hydrocarbons, these values clearly reveal the wide variation in the quantity and type of the non-hydrocarbon content of the gases.

TABLE 1.—*Natural Gases of the United States.*

		Analysis					
Locality	Type of Gas	CH_4	C_2H_6 and Higher	CO_2	N_2	He	H_2S
Pittsburgh, Pa.	City gas	84.7	13.7	—	1.6	—	—
Cleveland, O.	" "	80.5	18.2	—	1.3	—	—
Cincinnati, O.	" "	79.8	19.5	—	0.7	—	—
Columbus, O.	" "	80.4	18.1	—	1.5	—	—
Bartlesville, Okla.	" "	92.4	3.1	1.4	3.1	—	—
Kansas City, Kan.	" "	84.1	5.7	0.8	8.4	—	—
Fort Worth, Ark.	" "	51.5	10.2	—	38.3	—	—
Los Angeles, Calif.	" "	77.5	16.0	6.5	0.0	—	—
Little Rock, Ark.	" "	96.7	—	1.0	2.3	—	—
Monroe, La.	" "	94.7	2.8	0.2	2.3	—	—
De Soto, La.	Dry gas	97.3	—	0.4	2.3	—	—
Elm Grove, La.	" "	98.7	—	0.2	0.1	—	—
Fort Smith, Ark.	" "	99.2	—	0.2	0.6	—	—
Glasgow, Ky.	Sulphurous gas	23.6	69.7	—	3.8	—	2.9
Olney, Ill.	"	37.5	59.6	—	1.7	—	1.2
Lower Oriskany Sand, Pa.	"	98.8	0.3	—	0.1	—	0.8
McKittrick, Calif.	Special types	66.2	1.0	30.4	2.4	—	—
Eureka, Kansas	"	51.8	—	0.2	46.4	1.50	—
Dexter, Kansas	"	14.9	0.4	—	82.7	1.84	—
Randall Co., Texas	"	14.7	—	(trace)	85.3	—	—

A number of complete analyses of various American natural gases have been made by Burrell, Seibert, and Robertson,[19] Shepherd,[20] Schaufelberger,[21] and

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[16] Hopkins, *Ind. Eng. Chem.*, 1930, **22**, 502.

[17] Bruun, *J. Chem. Education*, 1931, **8**, 1930; *Chem. Abs.*, 1931, **25**, 5974; analytical methods are discussed in Chapter 49.

[18] Garner and Miller, *Oil and Gas J.*, 1927, **26** (4), 137, 140; *Chem. Abs.*, 1927, **21**, 2782.

[19] *Bur. Mines, Tech. Paper* 104, 1915; *Chem. Abs.*, 1916, **10**, 266. See also Fowler, *Bur. Mines Information Circular* 6737, 1933; *Chem. Abs.*, 1933, **27**, 4912.

[20] *Bur. Standards J. Research*, 1929, **2**, 1145; *Oil and Gas J.*, 1929, **28** (6), 48; *Chem. Abs.*, 1929, **23**, 4562.

[21] *Oil and Gas J.*, 1930, **29** (16), 46; *Chem. Abs.*, 1930, **24**, 5995.

Podbielniak.[22] In all of these, low-temperature fractionation methods were employed to separate and estimate the individual hydrocarbons. The development of analytical methods involving careful low-temperature fractionation through a special column has been greatly advanced by the work of Podbielniak.[23] Typical analyses of various gases in the Podbielniak apparatus are given in Table 2.

TABLE 2.—*Natural Gas Analyses.*
(Per cent by volume)

Gas	Methane	Ethane	Propane	n-Butane	Isobutane	Pentanes and Higher Hydrocarbons
Wet gas	65.7	12.4	11.3	5.0	1.8	3.9
Dry gas	77.6	6.9	10.1	4.8		0.6
Wet gas	53.3	7.3	17.7	10.9	3.3	7.5
Residual gas	87.6	6.9	4.7	0.3	0.2	0.3
Natural gasoline (liquid)	—	3.8	6.7	19.7	5.2	64.6

It is not necessary to include a large number of complete analyses of various American gases in this discussion, since the composition of such gases depends very largely on immediate operating conditions and may vary somewhat from day to day. As might be expected, the dry gases show a greater constancy of composition over extended periods than wet gases.

The natural gases of Canada, particularly those of the provinces of Ontario and Alberta, have been considered from the point of view of their possible industrial utilization.[24] Rosewarne[25] gave the following typical analyses by low-temperature fractionation of gases from wells in the Turner Valley field of Alberta during 1930. (See Table 3.)

TABLE 3.—*Natural Gases from Turner Valley, Alberta.*
Analysis (per cent by volume).

Well	He	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12} and Higher Hydrocarbons
Advance No. 5...........	0.007	87.2	6.6	3.7	1.7	0.8
Dalhousie No. 5.........	0.009	85.0	7.4	3.8	2.1	1.7
Royalite No. 6...........	0.009	88.5	6.5	3.3	1.3	0.5
Royalite No. 17..........	trace	88.3	6.2	3.4	1.5	0.6
Calgary city gas	—	89.1	5.5	3.2	1.3	0.9
Stabilizer gas	—	25.3	13.6	29.4	23.3	8.4
Stabilizer gas	—	36.3	20.7	15.7	16.9	10.4

Few analyses of natural gases from other parts of the world have been reported. However, some Russian natural gases have been analyzed by low-temperature fractionation methods by Sokolov.[26] The results are given in Table 4.

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[22] *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 177; *Chem. Abs.*, 1931, 25, 2613; *Refiner*, 1929, 8 (3), 55; *Chem. Abs.*, 1929, 23, 3128; *Oil and Gas J.*, 1930, 29 (20), 235; *Chem. Abs.*, 1930, 24, 5992; see also Chapter 49.

[23] *Loc. cit.*

[24] Elworthy, *Canadian Dept. Mines Summary Report* 586, 1921, 56; *Chem. Abs.*, 1923, 17, 2636; Hume, *Can. Mining J.*, 1930, 51, 991; *Chem. Abs.*, 1931, 25, 190; Harkness, *Ann. Rept. Ont. Dept. Mines*, 1930, 38 (5), 1; *Chem. Abs.*, 1932, 26, 281.

[25] *Canadian Dept. Mines Mem. Series* 43, 1930; *Chem. Abs.*, 1931, 25, 578; see also Rosewarne and Offord, *Canadian Dept. Mines, Mines Branch Rept.* 725, 1933, 92; *Chem. Abs.*, 1933, 27, 3317; *Canadian Dept. Mines, Mines Branch Rept.* 721, 1932, 109; *Chem. Abs.*, 1932, 26, 2848.

[26] *Neft. Khoz.*, 1930, 18, 793; *Chem. Abs.*, 1931, 25, 397.

Low-temperature fractionations of various Russian natural gases have also been made by Nametkin and others,[27] and the composition of gases from the Makat and Baku oilfields has been reported by Trebin and Luchinskii [28] and by Rabinovich,[29] respectively. The gases from the neighborhood of Baku (Apsheron peninsula) frequently possess a high content of carbon dioxide. Some Italian natural gases have been examined by Levi, Padovani, and Busi [30] and those of Poland by Kling, Beckówna and Kirschbaum.[31]

TABLE 4.—*Russian Natural Gases.*
Analysis (per cent by volume).

Field	Air	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	Higher
Surakhany	1.0	18.2	77.5	2.0	0.8	0.5	—
Grozny	1.0	—	51.8	10.7	25.1	8.8	1.9
Dagestanskie Ogni	1.0	7.5	89.0	1.9	0.6	0.6	—

Utilization of Natural Gas. Natural gas is used on a very large scale for the manufacture of carbon black.[32] Advances in our knowledge of the chemical transformations of the simpler paraffin hydrocarbons lead to the belief that natural gas is a chemical raw material of the highest promise, though so far only the fringe of this vast subject has been explored.[33]

The main use for natural gas is as a domestic and industrial fuel.[34] The wet gases, however, are now invariably treated for the recovery of liquid constituents, which include the paraffin hydrocarbons from butane [35] up to and including octane. The liquid obtained by stripping wet natural gas is called natural-gas gasoline and is an important source of volatile constituents for blending with gasoline obtained by distillation of crude petroleum or by cracking. When mixed with heavier naphtha, it yields a mixture comparable with the straight-run product.

The extraction of gasoline from natural gas is effected on a large scale by three distinct methods: (1) compression, (2) absorption in oil, and (3) adsorption on solids, such as activated charcoal.[36] The properties of gasolines prepared by these processes differ to some extent, the compression process yielding a very volatile product. Before blending such natural gasoline with straight-run gasoline it is necessary, therefore, to remove some of the more volatile ("wild") constituents. This process, yielding a gasoline of definite vapor pressure, is called stabilization. The most objectionable constituent from the point of view of volatility is propane, which must be removed almost entirely to obtain a satisfactory blending material. The stabilization process, which consists essentially of fractional distillation under pressure, also removes butane.

Huge amounts of liquefied propane and butanes thus produced are now being utilized for a number of purposes, particularly as a fuel for domestic and indus-

[27] Nametkin, Zabrodina, Karkonas, Kursanov, Sokolov, and Uspenskii, *Zhur. Prikladnoi Khim.*, 1931, 4, 335; *Chem. Abs.*, 1932, 26, 281. Sarkisyantz, *Prirodnuie Gazui.*, 1931, 2, 129; Uspenskaya, *Prirodnuie Gazui.*, 1931, 2, 171; Golubyatnikov, *Prirodnuie Gazui.*, 1931, 2, 139; *Chem. Abs.*, 1932, 26, 1416.

[28] *Neft. Khoz.*, 1930, 18, 789; *Chem. Abs.*, 1931, 25, 397.

[29] *Azerb. Neft. Khoz.*, 1931 (6), 37; *Chem. Abs.*, 1932, 26, 579.

[30] *Ann. chim. applicata*, 1931, 21, 245; *ibid.*, 1932, 22, 380; *Chem. Abs.*, 1931, 25, 5541; *ibid.*, 1932, 26, 5730.

[31] *Przemysl Naftowy*, 1932, 7, 317, 340; *Chem. Abs.*, 1932, 26, 5731.

[32] See Chapters 6 and 7.

[33] A review of the treatment of natural gases for the production of various products is given by Hoffman, *J. Inst. Pet. Tech.*, 1933, 19, 549; Frolich and Wiezevich, *Ind. Eng. Chem.*, 1932, 24, 13.

[34] Discussions of natural gas as a fuel are given by Bending, *Combustion*, 1931, 3 (1), 21; *Chem. Abs.*, 1932, 26, 281; *Gas Age-Record*, 1931, 68, 258, 311; *Chem. Abs.*, 1931, 25, 5969; Rogers, *Gas Age-Record*, 1931, 67, 987; *Chem. Abs.*, 1932, 26, 281.

[35] Butane is normally gaseous but behaves as a liquid when sufficient higher-boiling material is present to suppress its vapor pressure.

[36] See Shellshear, *Chem. Eng. Mining Review*, 1933, 25, 323; *Chem. Abs.*, 1933, 27, 4904.

trial consumption.[37] So-called liquefied petroleum gas, consisting of propane, n-butane and isobutane, which are gaseous under normal conditions but liquid under pressure, is now transported in steel cylinders and in special tank cars under pressure. This material is useful not only as an industrial and domestic fuel in districts remote from towns, but it can also be used for enriching manufactured gas and water gas [38] and as a substitute for acetylene in welding. From a chemical standpoint, liquefied petroleum gases, available in large quantities at a relatively low cost, appear to be ideal raw materials for the manufacture of certain organic chemicals. The available supply of these liquefied gases is very great —it has been estimated that the natural gasoline industry of the United States could easily produce 5,000,000 gallons of propane and 3,500,000 gallons of the butanes daily without appreciable diminution of natural gasoline supply.[39]

Because of its freedom from vaporization difficulties at low temperatures, propane is finding special application for domestic purposes, and the use of commercial butane as a carbureting agent in gas manufacture is one of the outstanding developments in the gas industry.[40] Liquefied petroleum gases have been proposed for the extraction and refining of rosin and gums [41] and for the purification of oils and asphalts.[42] The gases, particularly propane, can be used also in refrigerating equipment.[43] Pentane has been suggested for treatment of paper preliminary to subsequent impregnation with viscous materials for the manufacture of insulation.[44] Methane has been investigated as a fuel for motor-driven vehicles, the operating results being favorable.[45] An explosive, consisting of an oxidizing agent, a liquefied volatile hydrocarbon and an absorbent, which loses its power soon after being loaded into a bore-hole, has been proposed by Wulff.[46]

In separating a condensate from a gas by compression or adsorption, the efficiency of separation is increased if a substance having a lower boiling point than any other constituent of the condensate is added.[46a] Thus a use is found for propane in effecting a more efficient separation of benzine from casinghead gas. The propane is subsequently removed from the condensate and again utilized.

Natural gas is also a raw material for the manufacture of hydrogen.[47] For this purpose, the gas is heated to a high temperature (usually about 1000° C.) to decompose the hydrocarbons into their elements. The thermal decomposition of hydrocarbons is discussed more fully in Chapters 2 and 7.

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[37] Heavner, *Oil and Gas J.*, 1930, **29** (6), 38, 148; *Chem. Abs.*, 1930, **24**, 3884; Van der Pyl, *Gas Age-Record*, 1930, **66**, 265; *Chem. Abs.*, 1930, **24**, 5987; Anon., *Proc. Am. Gas Assoc.*, 1930, 1928; Dieterle, *ibid.*, 1930, 1623; *Chem. Abs.*, 1931, **25**, 4686; Brooks, *World Petroleum*, 1931, **2** (6), 380; *Chem. Abs.*, 1932, **26**, 287; Legatski, *Oil and Gas J.*, 1932, **31** (1), 44; *Chem. Abs.*, 1932, **26**, 5405; Lindsey, *Western Gas*, 1932, **8** (8), 54; *Chem. Abs.*, 1932, **26**, 5403; Thomas, *Fuels and Steam Power*, 1930, **52** (12), 143; *Chem. Abs.*, 1930, **24**, 5471. For the use of liquefied petroleum gases in the textile industry see Van Note, *Textile World*, 1931, **80**, 1408; *Chem. Abs.*, 1932, **26**, 311.

[38] Eddy, Fischer, Duesler, Hitz, Schell, *Proc. Am. Gas Assoc.*, 1929, 1299-1327; *Chem. Abs.*, 1930, **24**, 3883.

[39] Thomas and Setrum, *Oil and Gas J.*, 1928, **27** (22), 330; *Chem. Abs.*, 1929, **23**, 2275; Alden, *Amer. Pet. Inst. Bull.*, 1929, **10** (2), Sect. II, 86; *Chem. Abs.*, 1930, **24**, 1728.

[40] Campbell, *Chem. Markets*, 1926, **26**, 147; Thomas, *Fuels and Steam Power*, 1930, **52** (12), 143; *Chem. Abs.*, 1930, **24**, 5471; Eddy, Fischer, Duesler, Hitz and Schell, *Proc. Am. Gas Assoc.*, 1929, 1299; *Chem. Abs.*, 1930, **24**, 3883; Harlow and Benz, *Fuels and Furnaces*, 1930, **8**, 83; *Chem. Abs.*, 1930, **24**, 1721; Setrum, *J. Western Soc. Eng.*, 1930, **35**, 448; *Chem. Abs.*, 1931, **25**, 1058; Setrum, *Ind. Eng. Chem.*, 1931, **23**, 1190; Hough, *Gas Age-Record*, 1930, **66**, 383; *Chem. Abs.*, 1930, **24**, 5977.

[41] Humphrey, U. S. Patent 1,806,973, May 26, 1931; assigned to Hercules Powder Co.; *Brit. Chem. Abs.* **B**, 1932, 235. Little, U. S. Patent 1,762,785, June 10, 1930; assigned to Arthur D. Little, Inc.; *Chem. Abs.*, 1930, **24**, 3898.

[42] Atwell, British Patent 390,222, 1931; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1933, 456; I. G. Farbenindustrie A.-G., British Patent 389,113, 1931; *Brit. Chem. Abs.* **B**, 1933, 378; Nobel, U. S. Patent 1,868,211, July 19, 1932; assigned to Bataafsche Petroleum Maatschappij; *cf.* Aschan, *Chem.-Ztg.*, 1927, **51**, 4; *Chem. Abs.*, 1928, **22**, 1032.

[43] Nelson, U. S. Patent 1,822,109, Sept. 8, 1931; assigned to Hoover Co.; *Chem. Abs.*, 1931, **25**, 5942.

[44] Bataafsche Petroleum Maatschappij, British Patent 381,448, 1932; *Chem. Abs.*, 1933, **27**, 5125.

[45] Bronn, *Brennstoff-Chem.*, 1931, **12**, 27, 45; *Chem. Abs.*, 1931, **25**, 1654; Klinkhardt, *Gas u. Wasserfach*, 1932, **75**, 495; *Chem. Abs.*, 1932, **26**, 4438.

[46] U. S. Patent 1,772,695, Aug. 12, 1930; *Brit. Chem. Abs.* **B**, 1931, 418.

[46a] Bataafsche Petroleum Maatschappij, British Patent 355,413, 1929; *Brit. Chem. Abs.* **B**, 1931, 1036.

[47] Rosenstein, *World Petroleum*, 1932, **3** (1), 31; *Chem. Abs.*, 1932, **26**, 6100; see also Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 1930, 759.

As previously stated, the liquefied petroleum gases consist of propane, n-butane, and isobutane. Propane can be easily separated on a large scale by efficient fractionation and with modern equipment the separation of butane and isobutane can also be accomplished. Such a separation, therefore, makes these three paraffin hydrocarbons available for purely chemical utilization.

NATURAL-GAS GASOLINE

Natural-gas gasoline, or casinghead naphtha, is the liquid hydrocarbon mixture extracted from natural gas by compression,[48] absorption in oil,[49] or adsorption on solids.[50] It is distinguished from straight-run products by its higher volatility and lower boiling range. In general, it consists of the lower members of the paraffin series from propane up to octane, though propane should be absent from the stabilized product.[51] Examination of samples of natural gasoline from many localities in Texas, Oklahoma, Kansas, Kentucky, Ohio, and West Virginia has shown that they all contain substantial proportions of the pentanes, of which three chemical individuals exist:

Pentanes	Boiling Point ° C. at 760 mm.[52]
Normal pentane $CH_3(CH_2)_3CH_3$	36.2°
Isopentane $(CH_3)_2CH.CH_2.CH_3$	28.0°
Tetramethylmethane $(CH_3)_2C(CH_3)_2$	9.5°

Natural gasolines contain from 20 to 40 per cent of normal and isopentane but tetramethylmethane (neopentane) is the least abundant, having been found to the extent of only 2 per cent in many natural-gas gasolines from Texas and West Virginia. Normal butane, boiling at 0° C., is present in natural-gas gasoline in substantial amounts but no hydrocarbon occurs boiling between 0° C. and 28° C. with the exception of traces of tetramethylmethane. Of the hydrocarbons boiling above 36° C. about 10 per cent consists of hexanes boiling at 58° C. (diisopropyl) and 62° C. (dimethylpropylmethane) with only a trace of trimethylethylmethane boiling at 49° C. According to Ayres,[53] natural-gas gasoline contains no unsaturated hydrocarbons and no cyclic hydrocarbons boiling below the hexanes.

The composition of a typical American natural-gas gasoline has been investigated by Anderson and Erskine.[54] The sample was first separated into four fractions (each with boiling ranges of about 20° C.) in the neighborhood of the boiling points of the normal paraffins of from five to eight carbon atoms. Three distillations of the pentane fraction with a regulated temperature still-head resulted in the isolation of isopentane (boiling point, 27.8°-28.3° C.) and n-pentane (boiling point, 35.5°-36.0° C.). From the hexane fraction, 2-methylpentane (isohexane) and n-hexane were obtained by a series of four distillations. Similarly, 2-methylhexane (isoheptane) and n-heptane were separated from the heptane fraction. Table 5 gives the approximate composition of the natural-gas gasoline.

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[48] Pence, *Oil and Gas J.*, 1930, **29** (8), 168; *Chem. Abs.*, 1930, **24**, 4620; Shellshear, *Chem. Eng. Mining Rev.*, 1933, **25**, 323; *Chem. Abs.*, 1933, **27**, 4904; Wells, *Petroleum Eng.*, 1930, **2** (3), 96; *Chem. Abs.*, 1931, **25**, 3475.

[49] Chatfield, *Natl. Petroleum News*, 1930, **22** (12), 90; *Chem. Abs.*, 1930, **24**, 4620; Sharples, U. S. Patent 1,766,195, June 24, 1930; assigned to Sharples Specialty Co.; *Chem. Abs.*, 1930, **24**, 4146. For determining the rates of solution of gases in each other and in oils see Lacey, *Oil and Gas J.*, 1931, **30** (8), 15, 118; **30** (9), 68, 114, 116; *Chem. Abs.*, 1932, **26**, 1103; Pomeroy, Lacey, Scudder and Stapp, *Ind. Eng. Chem.*, 1933, **25**, 1014; Uehara, *J. Chem. Soc. Japan*, 1932, **53**, 931; *Chem. Abs.*, 1933, **27**, 700; Matheson and Cummings, *Ind. Eng. Chem.*, 1933, **25**, 723.

[50] Moore, *Fuel*, 1931, **10**, 436; Magnus and Windeck, *Z. phys. Chem.*, 1931, **153A**, 113; *Chem. Abs.*, 1931, **25**, 2616; Stenzel, *J.A.C.S.*, 1932, **54**, 870.

[51] Smith, *Oil and Gas J.*, 1930, **29** (4), 38, 94; *Chem. Abs.*, 1930, **24**, 3892. In 1930 there were 1035 natural-gasoline plants in the United States with a capacity of over 10 million gallons per day, according to Hopkins and Seeley (U. S. Bureau of Mines Information Circular 6279, 1930; *Chem. Abs.*, 1930, **24**, 4620). For economics of the industry see also Mayer, *Petroleum Z.*, 1931, **27**, 464; *Chem. Abs.*, 1931, **25**, 5975.

[52] International Critical Tables, National Research Council, McGraw-Hill Book Co., Inc., New York, 1926, **1**, 193.

[53] *Ind. Eng. Chem.*, 1929, **21**, 899.

[54] *Ind. Eng. Chem.*, 1924, **16**, 263.

TABLE 5.—*Natural-Gas Gasoline.*

Constituents	Per Cent by Volume
Propane and Butanes	20
Isopentane	13
n-Pentane	17
2-Methylpentane	9
n-Hexane	15
2-Methylhexane	8
n-Heptane	12
Octanes	4
Absorption oil	2

In addition to paraffin hydrocarbons, which form the preponderating constituents of casinghead gasoline, small proportions of aromatic hydrocarbons (as well as the simple naphthenes) are frequently present. Erskine[55] found benzene, toluene, and m-xylene even in a highly paraffinic Pennsylvania natural-gas gasoline. Gases which have been in contact with highly aromatic crudes such as those of Borneo (Koetei) and Rumania (Dacic) are likely to contain large amounts of benzene and its immediate homologues. Similarly, the simple naphthenes (cyclopentane and cyclohexane and their immediate homologues) are probably present in gases derived from highly naphthenic crudes such as those of Southern Russia.[56]

A condensate obtained from pipe lines of the Terrebonne gas fields near Houma, La., having a much higher boiling range and specific gravity than ordinary casinghead naphtha, has been investigated by Coates and Tims.[57] A study of the fraction of this condensate boiling at 215°-217° C. and having the formula $C_{12}H_{22}$ showed it to be identical with a similar fraction from a crude oil of Jennings, La., studied by Coates[58] in 1906. It was believed that alkyl derivatives of dicyclopentyl were present.

CRUDE PETROLEUM

Disregarding the non-hydrocarbon constituents, which on the average represent only a very small percentage of the total, crude petroleum is essentially a complex mixture of hydrocarbons of all classes and degrees of complexity. Since, from a theoretical standpoint, there is an enormous number of possible individual hydrocarbons possessing molecular weights up to 1000,[59] it is not surprising that the physical and chemical properties of crude petroleums from different sources vary considerably.

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[55] *Ind. Eng. Chem.*, 1926, 18, 722.

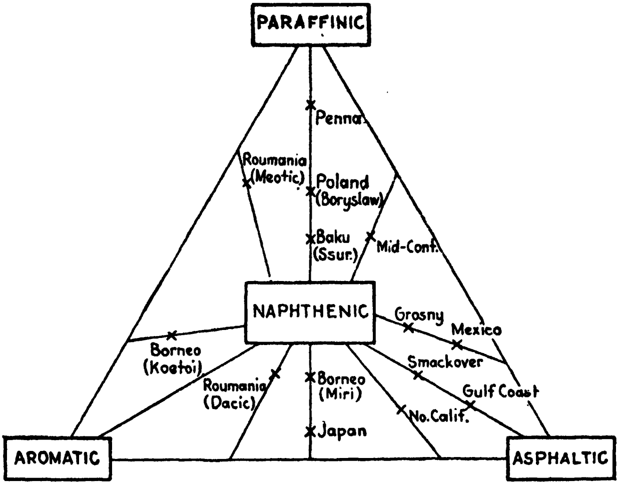
[56] Analysis of a Grozny natural gasoline is reported by Isaev, Egorov and Grigoriev, *Grozn. Neft.*, 1932, 2 (3-4), 49-53; *Brit. Chem. Abs.* B, 1933, 134.

[57] *Ind. Eng. Chem.*, 1922, 14, 219.

[58] *J.A.C.S.*, 1906, 28, 384.

[59] Henze and Blair (*J.A.C.S.*, 1931, 52, 3077) have shown that there are 62,491,178,805,831 isomeric paraffins containing 40 carbon atoms.

Crude petroleums have been roughly classified in the past as paraffin base, naphthene base, or asphalt base. The first two classes contain a preponderance of paraffin and naphthene hydrocarbons, respectively, in their lower fractions, whereas the asphalt base crudes, as their name implies, contain asphaltic substances (i.e., high molecular weight hydrocarbons with relatively low hydrogen content, as well as high molecular weight oxygenated substances) in their higher fractions. All possible variations among these classes are known, crude petroleums containing both paraffins and asphaltic substances being termed "mixed-base" oils. However, from a purely chemical standpoint this system of classification is quite inadequate since even the most paraffinic crudes contain cyclic hydrocarbons in increasing amount as the boiling point of the fractions rises.



Courtesy McGraw-Hill Book Co., Inc.

FIG. 1.—Diagram Showing Probable Composition of Various Crude Oils. (Gruse.)

In the system used by Gruse,[60] crude petroleums are classified as paraffinic, aromatic, and asphaltic, the naphthenes being present in varying proportions in all classes. To illustrate the probable composition of various crudes, Gruse employed the triangular diagram given above (Fig. 1).

The detection of individual hydrocarbons in crude petroleum is one of the most difficult problems of organic chemistry. Apart from a few special chemical methods of attack, strictly limited in their scope, the only direct methods of investigation available are fractional distillation and fractional crystallization, both of which are tedious and time-consuming and none too dependable.

Fractional distillation of the low molecular weight hydrocarbons of petroleum has made possible the definite identification of a few of the simpler members. The differences in boiling points (and consequently vapor pressures) of hydrocarbons diminish with increasing molecular weight, and at the same time the number of possible isomers increases rapidly.[61] In addition to this difficulty, the

[60] Gruse, "Petroleum and its Products," McGraw-Hill Book Co., Inc., New York, 1928, 3.
[61] See Henze and Blair, *loc. cit.*

separation of the normally liquid hydrocarbons is complicated still further by the formation of constant-boiling mixtures. Two isomers or two totally different hydrocarbons may possess the same boiling point, consequently the isolation of a fraction of constant boiling point from fractions other than the lowest-boiling ones is by no means an indication of the presence of a pure chemical individual. Much of the older work on the identification of pure chemical individuals in petroleum by fractional distillation methods is unreliable for these reasons and unwarranted conclusions were often drawn from such totally inadequate data. Of the large number of hydrocarbons which are said to have been isolated from petroleum, only a few have been indubitably proved to be present. Though many of the others may, and very likely do, actually occur in various crudes, the evidence adduced for their supposed presence is, in most cases, utterly worthless. Washburn[62] described tests for purity and evidence of identity for hydrocarbons isolated from petroleum and recommended that at least five properties—refractive index, density, boiling point, freezing point, and halogenation behavior—should be reported before identification is established. Esau[63] observed that the purity of hydrocarbons could be tested by measuring the change of temperature produced on submitting them to the action of short electrical waves (of frequencies of the order of 10^8 hertz).

Except in a very few cases it is a matter of the greatest difficulty to separate any hydrocarbon of more than six or seven carbon atoms in a pure state from crude petroleum by fractional distillation. Other methods of isolating pure hydrocarbons from petroleum are available in special cases. Thus, the higher paraffins are solids which may be resolved by laborious fractional crystallization. Certain solvents appear to possess selective solvent properties towards particular types of hydrocarbons, though the separation of pure individuals by such means is difficult. Nevertheless, selective solvent action may be employed to concentrate certain types of hydrocarbons into one or more fractions. An example of this solvent selectivity is the large-scale use of liquid sulphur dioxide to extract aromatic hydrocarbons (together with some unsaturated hydrocarbons if they are present) from kerosenes. Furthermore, certain methods have been developed for roughly determining the various classes of hydrocarbons in gasoline (and to a smaller extent in kerosene) but they are not applicable to fractions boiling above this range.

STRAIGHT-RUN GASOLINES

Straight-run gasoline, the lowest fraction obtained from crude petroleum by straight distillation, is a mixture of hydrocarbons of the paraffin, benzene, and naphthene (cycloparaffin) series. Olefins have been reported from time to time but careful work has indicated that these substances are present in small quantities only, as already mentioned, and the proportions probably depend upon the conditions of distillation.

The gasolines produced from American crudes, especially from the Eastern gasolines, and to a lesser extent from the Mid-Continent ones, are paraffinic in nature. The asphaltic oils of the Gulf Coast and California apparently produce gasolines with larger proportions of naphthene hydrocarbons (and dissolve in sulphuric acid to a greater extent) than the two mentioned. Although all American gasolines probably contain some aromatic hydrocarbons (only in small quantities in most cases, especially Eastern gasolines), some from California, on the other hand, contain high percentages of aromatics.[64] Table 6 gives analyses (in terms of classes of hydrocarbons) of various straight-run gasolines of the United States.[65] In view of the controversy as to the adequacy of the methods employed, these data should be considered as only approximate.

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[62] *Ind. Eng. Chem.*, 1930, 22, 985.

[63] British Patent 345,464, 1930; *Brit. Chem. Abs.* B, 1931, 579. Also French Patent 691,306, 1930; *Chem. Abs.*, 1931, 25, 962.

TABLE 6.—*American Straight-Run Gasolines.*

Gasoline Source	Composition, Per Cent by Volume Naphthenes	Aromatics	Unsaturates	Paraffins
Pennsylvania	13.0	6.9	2.2	77.9
Pennsylvania	1.2	4.2	2.3	92.3
Pennsylvania	23.4	0.0	1.3	75.3
Pennsylvania	23.2	0.0	4.0	73.6
Pennsylvania	11.7	4.9	2.9	80.5
Oklahoma (Cushing)	23.7	4.9	1.6	69.8
Oklahoma (Cushing)	17.9	3.6	3.7	74.8
Oklahoma (Cushing)	26.2	0.0	2.9	70.9
Oklahoma (Seminole)	23.0	4.5	3.4	69.1
Kentucky	23.1	2.8	5.8	68.3
Kentucky (Somerset)	20.6	5.3	3.8	70.3
California	34.9	2.8	5.1	57.2
California	41.2	0.8	2.3	55.7
Kansas	20.3	0.4	2.7	76.6
Arkansas (Smackover)	14.5	11.3	7.9	66.3
Texas (Refugio)	23.1	8.7	2.2	66.0
Texas	27.4	6.0	3.2	69.4
Texas	25.8	2.5	3.2	68.5
Texas	24.7	1.2	3.7	70.4
Texas (Van Zandt)	0.0	2.9	1.7	95.4
Michigan (Mt. Pleasant)	7.4	4.5	2.9	85.2

In other parts of the world, gasolines of widely divergent chemical compositions are obtained.[66] Gasolines with large proportions of naphthene hydrocarbons are produced from the crudes of South Russia (Surakhany), Rumania (Dacic), Japan, and certain parts of Borneo. According to Kewley,[67] Miri (Borneo) benzine consists of 80 per cent of naphthenes, 15 per cent of paraffins, and only 5 per cent of aromatic hydrocarbons. On the other hand, the gasoline from Koetei

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[64] Burrell, *Ind. Eng. Chem.*, 1928, **20**, 602.

[65] Egloff, Bollman and Levinson, *J. Phys. Chem.*, 1931, **35**, 3492; *Chem. Abs.*, 1932, **26**, 1255; also, Egloff, Nelson and Truesdell, *Oil and Gas J.*, 1931, **29** (39), 38; *ibid.*, 1931, **29** (40), 30; *Chem. Abs.*, 1931, **25**, 3469, 3473. Analyses of gasolines are also given by Chantler, *Canadian Dept. Mines, Mines Branch Rept.* **725**, 1933, 149; *Chem. Abs.*, 1933, **27**, 3322.

[66] For the analyses of Japanese petroleums see Mizuta, *J. Soc. Chem. Ind. Japan*, 1931, **34**, Suppl. binding 288; *Chem. Abs.*, 1931, **25**, 5976; *J. Soc. Chem. Ind. Japan*, 1931, **34**, Suppl. binding 330; *Chem. Abs.*, 1932, **26**, 1425; *J. Soc. Chem. Ind. Japan*, 1932, **35**, 80B; *Chem. Abs.*, 1932, **26**, 3366; *J. Soc. Chem. Ind. Japan*, 1932, **35**, Suppl. binding 157; *Chem. Abs.*, 1932, **26**, 4458; *Proc. World. Eng. Cong. Tokyo*, 1931, **31**, 31; *Chem. Abs.*, 1931, **25**, 5548; *J. Soc. Chem. Ind. Japan*, 1932, **35**, Suppl. binding 470; *Chem. Abs.*, 1933, **27**, 1492; Kobayaski, *J. Soc. Chem. Ind. Japan*, 1931, **34**, Suppl. binding 289; *Chem. Abs.*, 1931, **25**, 5975; *J. Soc. Chem. Ind. Japan*, 1932, **35**, Suppl. binding 107; *Chem. Abs.*, 1932, **26**, 3655; *J. Soc. Chem. Ind. Japan*, 1932, **35**, Suppl. binding 426; *Chem. Abs.*, 1933, **27**, 183; Iimori and Kikuchi, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1929, **8**, 984; *Chem. Abs.*, 1930, **24**, 4922; Akita, *Trans. II World Power Conf.*, 1930, **8**, 21; *Brit. Chem. Abs.* **B**. 1932, 168. Chinese petroleum analyses have been reported by Chin, *Science (China)*. 1932, **16**, 1049; *Chem. Abs.*, 1932, **26**, 5739. Analyses of Russian petroleums have been made by Postovski and Plyusnin, *J. Chem. Ind. (Russia)*, 1930, **6**, 776; *Chim. et ind.*, Special No. (March 1930). 196; *Chem. Abs.*, 1930, **24**, 5470; Bestushev and Malashkin, *Neft. Khoz.*, 1930, **18**, 965; *Chem. Abs.*, 1931, **25**, 402; Nametkin and Shakhnazarova, *Neft. Khoz.*, 1930, **19**, 290; *Chem. Abs.*, 1931, **25**. 402; Volf and Shevlyakov, *Azerb. Neft. Khoz.*, 1931 (9-10), 83-92; *Chem. Abs.*, 1932, **26**, 1425; Marko and Lapkin, *Bull. inst. recherches biol. univ. Perm*, 1932, **8**, 145; *Chem. Abs.*, 1933, **27**, 4063; Kligerman, *Azer. Neft. Khoz.*, 1932 (8-9), 59; *Chem. Abs.*, 1933, **27**, 184. Polish petroleums have been analyzed by Winkler, *Przemysl Chem.*, 1930. **14**, 1; *Chem. Abs.*, 1930, **24**, 4923; Szayna and Ehrlich, *Przemysl Naftowy*, 1932, **7**, 14; *Chem. Abs.*. 1932, **26**, 3094. Petroleums of Rumania have been analyzed by Casimir, Creanga and Dimitriu, *Allgem. österr. Chem. u. Tech.-Ztg.*, 1930, **48**, 57; *Chem. Abs.*, 1930, **24**, 3634; Gane and Zilisteanu-Gheorghiu, *Bull. soc. chim. Romania*, 1926, **8**, 3; *Chem. Abs.*, 1928, **22**, 3520. Analyses of petroleums from Japan have also been reported by Mizuta, *J. Soc. Chem. Ind. Japan*, 1933, **36**, Suppl. binding 330; *Chem. Abs.*, 1933, **27**, 4659; and from Russia by Bestushev, *Erdöl u. Teer*, 1931, **7**, 159; *Chem. Abs.*, 1931, **25**, 3816.

[67] *J. Inst. Pet. Tech.*, 1921, **7**, 219; *Chem. Abs.*, 1921, **15**, 3738.

(Dutch Borneo), which contains upwards of 40 per cent of aromatic hydrocarbons (as well as 26 per cent of paraffins and 35 per cent of naphthenes), was used as a source of toluene during the World War in the manufacture of TNT.[68]

The systematic work of Young and Thomas[69] led to the definite identification of n-pentane, isopentane, n-hexane, isohexane, n-heptane, and isoheptane in American petroleum. The presence of isomeric hexanes and heptanes was considered likely but not definitely proved in their work. Several of the higher paraffins were said to have been identified by fractionation methods but it is very doubtful whether the products obtained were pure. Other work in this connection is that of Brown and Carr,[70] who fractionated a straight-run gasoline from the Cabin Creek field up to the nonane fraction, using a semi-laboratory fractionating column and starting with 135 gallons of oil. Scores of fractions were obtained which had distillation curves with a semblance of flatness but pure compounds were not isolated. In addition to indications of the presence of butane, benzene, cyclopentane, toluene, isoheptane, and certain of the nonanes and decanes, fractions were identified having the boiling points of isopentane, n-pentane, isohexane, n-hexane, n-heptane, isooctane, n-octane, and n-nonane.

A study of the hexane fraction of an Oklahoma gasoline (straight-run) was made by Bruun and Hicks-Bruun.[71] Careful fractionation concentrated the hexanes into a series of constant-boiling mixtures. After the addition of methyl alcohol, refractionation yielded azeotropic mixtures of alcohol and the hexanes, all of which boiled below 58.7° C. The following isomers were separated: 2,3-dimethylbutane, 2- and 3-methylpentanes, and n-hexane but no 2,2-dimethylbutane. Later they isolated n-heptane[72] (boiling at 98.4° C.), n-decane[73] (boiling at 174.0° C.), 2-methylhexane[74] (boiling at 89.67° C.), and showed the probable presence of 2,2-dimethylpentane.[75]

Leslie and Schicktanz[76] separated pure n-octane from a fraction (boiling point, 100°-130° C.) of the same crude from Oklahoma, by a series of fractional distillations followed by fractional crystallizations at low temperatures. Treatment with chlorosulphonic acid was employed to obtain the purest product. Leslie[77] also isolated 2-methylheptane (boiling point, 117.2° C.) by crystallization from liquid methane. By fractionation of a Pennsylvania straight-run gasoline, Tongberg and Fenske[78] isolated 2-methylpentane (boiling at 60.3° C.), n-heptane (boiling at 98.4° C.), methylcyclohexane (boiling at 100.8°-100.9° C.), and n-octane (boiling at 125.2° C.).

The use of chlorosulphonic acid in the purification of normal paraffins is effective because hydrocarbons containing the grouping R_3CH are rapidly attacked whereas normal hydrocarbons (and also cyclohexane) are only slowly affected by the reagent.[79] Shepard, Henne, and Midgley[80] also applied this reagent to the isolation of normal paraffins in a pure state from closely cut gasoline fractions. A gasoline of about 70 per cent normal paraffin content was distilled into fractions which roughly represented the normal homologues. The fractions were then treated with chlorosulphonic acid until no further change of density occurred, and were subsequently redistilled through a spiral fractionating column with an efficient dephlegmator. In this way the eight normal paraffins from pentane to dodecane were obtained in a satisfactory state of purity, the freezing range for each fraction being less than 0.1° C.

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[68] Kewley, *J. Inst. Pet. Tech.*, 1921, 7, 215; *Chem. Abs.*, 1921, 15, 3738. The preparation of TNT from aromatic fractions of petroleum is discussed also by Mizuta, *J. Soc. Chem. Ind. Japan*, 1933, **36**, Suppl. binding 255; *Chem. Abs.*, 1933, **27**, 4064; Dănăilă and Popa, *Analele minelor din Romania*, 1925, **8**, 129; *Chem. Abs.*, 1925, **19**, 1771; Popla and Velculescu, *Bul. chim. soc. romana stiin.*, 1930, **33**, 1; *Brit. Chem. Abs.* **B**, 1932, 790.

[69] *J.C.S.*, 1897, **71**, 440.

[70] *Ind. Eng. Chem.*, 1926, **18**, 718.

[71] *Bur. Stand. J. Res.*, 1930, **5**, 933; *Chem. Abs.*, 1931, **25**, 2275.

[72] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1932, **8**, 525; *Chem. Abs.*, 1932, **26**, 3655.

[73] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1932, **8**, 583; *Chem. Abs.*, 1932, **26**, 4451.

[74] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1933, **10**, 465; *Brit. Chem. Abs.* **B**, 1933, 611.

[75] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1932, **9**, 53; *Chem. Abs.*, 1932, **26**, 5739.

[76] *Bur. Stand. J. Res.*, 1931, **6**, 377; *Chem. Abs.*, 1931, **25**, 2551.

[77] *Bur. Stand. J. Res.*, 1933, **10**, 609; *Chem. Abs.*, 1933, **27**, 4062.

[78] *Ind. Eng. Chem.*, 1932, **24**, 814.

[79] Aschan, *Ber.*, 1898, **31**, 1801; *Chem. Soc. Abs.*, 1898, **74** (1), 545; Young, *J.C.S.*, 1899, **75**, 172.

[80] *J.A.C.S.*, 1931, **53**, 1948; *Ind. Eng. Chem.*, 1930, **22**, 356.

Table 7 contains data for a number of paraffin fractions which have been isolated by fractional distillation from various gasolines.[80a] Some of these fractions approximate very closely the physical properties of the corresponding pure hydrocarbon.

The naphthene hydrocarbons of the gasoline fraction of petroleum consist mainly, if not entirely, of cyclopentane and cyclohexane homologues. It is possible that hydrocarbons possessing monocyclic carbon ring systems with other than 5 or 6 carbon atoms are also present to some extent, but the evidence adduced of their presence is not convincing. Midgley [81] was reported to have isolated a dimethylcyclobutane from a gasoline fraction of Californian petroleum, and Markownikow [82] obtained evidence of the presence of cycloheptane in a fraction (boiling at 115° to 120° C.) of a Caucasian petroleum. A considerable number of cyclopentane and cyclohexane hydrocarbons have been more or less positively identified in various gasoline fractions of crude petroleums. Cyclopentane itself was found by Markownikow [83] in the 48° to 57° C. fraction of a Caucasian petroleum, and by Young [84] in an American petroleum fraction. Cyclopentane appears to be present in many petroleums and has even been found in the highly paraffinic gasoline from Cabin Creek.[85] Methylcyclopentane has been found in Caucasian,[86] American,[87] Rumanian [88] and Japanese [89] petroleums. Hicks-Bruun and Bruun [90] isolated a pure specimen of methylcyclopentane from a fraction of a Mid-Continent petroleum by nitration of the accompanying benzene followed by distillation and fractional melting. A 1,1-dimethylcyclopentane (boiling at 87.5° C.) was later identified by them in this same petroleum.[91]

The presence of cyclohexane in a sample of American petroleum was demonstrated by Young.[92] As early as 1880, however, Beilstein and Kurbatow [93] showed that the lower fractions of Russian petroleum contain non-olefinic hydrocarbons of the formula C_nH_{2n}. Baeyer's synthesis of cyclohexane [94] led to the identification of this hydrocarbon (boiling point, 80° C.) in a Baku naphtha.[95] At about the same time a hydrocarbon boiling at 72° C. was isolated and proved to be the isomeric methylcyclopentane.[96] Fortey [97] isolated what was at first considered to be pure cyclohexane (boiling point, 80.8° C.) from a sample of Galician petroleum. It was afterwards found, however, that it could be partially

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[80a] This table compiled by Brown and Carr, *Ind. Eng. Chem.*, 1926, **18**, **718**.

[81] See Brooks, *Ind. Eng. Chem.*, 1924, **16**, 185; *cf.* Burrell, *ibid.*, 1928, **20**, 602.

[82] *J. Russ. Phys.-Chem. Soc.*, 1902, **34**, 917; *Chem. Zentr.*, 1903, 1, 568; *Chem. Soc. Abs.*, 1903, **84** (1), 239.

[83] *Ber.*, 1897, **30**, 975; *Chem. Soc. Abs.*, 1897, **72** (1), 329.

[84] *J.C.S.*, 1898, **73**, 906.

[85] Brown and Carr, *Ind. Eng. Chem.*, 1926, 18, 718.

[86] Markownikow, *Ber.*, 1897, **30**, 1223; *Chem. Soc. Abs.*, 1897, **72** (1), 401; *Ann.*, 1899, **307**, 344; *Chem. Soc. Abs.*, 1899, **76** (1), 799.

[87] Young, *J.C.S.*, 1898, **73**, 906.

[88] Poni, *Ann. acad. romane*, **23**; *Chem. Zentr.*, 1900, **2**, 452; *Chem. Soc. Abs.*, 1900, **78** (1), 617.

[89] Komatsu and Kusumoto, *Mem. Fac. Sci. Kyoto Imp. Univ.*, 1924, **7**, 77; *Chem. Abs.*, 1924, 18, 1562.

[90] *Bur. Standards J. Research*, 1931, **7**, 799; *Chem. Abs.*, 1932, **26**, 1423.

[91] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1933, **10**, 465; *Brit. Chem. Abs.* **B**, 1933, 611.

[92] *J.C.S.*, 1898, **73**, 907.

[93] *Ber.*, 1880, **13**, 1818, 2028; *Chem. Soc. Abs.*, 1881, **40** (1), 159.

[94] *Ber.*, 1893, **26**, 229; *Ann.*, 1893, **278**, 88; *Chem. Soc. Abs.*, 1893, **64** (1), 255.

[95] Markownikow, *Ber.*, 1897, **30**, 1222; *Chem. Soc. Abs.*, 1893, **64** (1), 255; *Ann.*, 1898, **302**, 1; *Chem. Soc. Abs.*, 1899, **76** (1), 22.

[96] Young, *J.C.S.*, 1898, **73**, 906.

[97] *J.C.S.*, 1898, **73**, 932.

TABLE 7.—*Fractions from Gasolines.*

Boiling Range ° C. at 760 mm.	Specific Gravity	Source	Investigator
Isopentane (2-Methylbutane) Fraction			
30.5–30.6	0.6220, 20°/15.5° C.	Cabin Creek, W. Va.	Brown and Carr [a]
30.2	——	Pennsylvania	Warren [b]
29–30	——	Ohio and Pennsylvania	Mabery and Hudson [c]
27.8–28.3	0.6248, 15.5°/15.5° C.	Natural-gas gasoline	Anderson and Erskine [d]
27.95	0.6380, 14° C.	Synthetic	Young and Thomas [e]
Normal-Pentane Fraction			
36.2–36.3	0.6309, 20°/15.5° C.	Cabin Creek	Brown and Carr [a]
37	0.6263, 17° C.	Russia	Markownikow [f]
35.5–36.0	0.6309, 15.5°/15.5° C.	Natural-gas gasoline	Anderson and Erskine [d]
36.3	0.6454, 0°/4° C.	Synthetic	Young and Thomas [e]
Isohexane (2-Methylpentane) Fraction			
61.1–61.2	0.6600, 20°/15.5° C.	Cabin Creek	Brown and Carr [a]
61	0.664	Pennsylvania and New Brunswick	Redwood [g]
61.3	0.676	Peru	Warren [h]
60.55–60.85	0.6728, 0°/4° C.	American Petroleum	Young and Thomas [e]
59.7–61.0	0.6613, 15.5°/15.5° C.	Natural-gas gasoline	Anderson and Erskine [d]
61.2	0.6762, 0° C.	Ohio and Canada	Mabery [i]
60.15–60.2	0.6580, 15°/15° C.	Synthetic	Risseghem [j]
Normal-Hexane Fraction			
68.9–69.0	0.6622, 20°/20° C.	Cabin Creek	Brown and Carr [a]
68.95	0.6771, 0°/4° C.	Appalachian Oil	Mabery [i]
68.95	0.6770, 0°/4° C.	American Petroleum	Young and Thomas [e]
67.9–69.2	0.6767, 15.5°/15.5° C.	Natural-gas gasoline	Anderson and Erskine [d]
Normal-Heptane Fraction			
98.6–98.7	0.6893, 20°/20° C.	Cabin Creek	Brown and Carr [a]
98.4	0.7018, 0°/4° C.	American Oil	Young and Thomas [e]
98.25–98.45	0.6829, 20° C.	Rangoon	Brown and Carr [a]
97.5–99	——	American Oil	Schorlemmer [k]
96–97	——	Ohio	Mabery [i]
98.2–99.3	0.7117, 15.5°/15.5° C.	Natural-gas gasoline	Anderson and Erskine [d]
98.43	0.7005, 0°/4° C.	Synthetic	Thorpe [l]
Isooctane (4-Methylheptane) Fraction			
117.9–118.1	0.7166, 20°/15.5° C.	Cabin Creek	Brown and Carr [a]
118	0.7217	Synthetic	Clarke [m]
Normal-Octane Fraction			
124.3–124.4	0.7123, 20°/20° C.	Cabin Creek	Brown and Carr [a]
124.7	0.7068, 15°/15° C.	Sumatra	Clarke [m]
121	0.732, 12.1° C.	American Oil	Lemoine [n]
124–125	0.7134	Ohio	Mabery and Hudson [c]
Normal-Nonane Fraction			
150.2–150.9	0.7380, 20°/15.5° C.	Cabin Creek	Brown and Carr [a]
150.8	0.7555	Pennsylvania	Warren [h]
151		Ohio	Mabery [i]

[a] *Ind. Eng. Chem.*, 1926, **18**, 718.

[b] *Mem. Am. Acad.*, 1867, **9**, 135; *Amer. Chem. J.*, 1868, (2) **45**, 262.

[c] *Proc. Am. Acad. Arts Sci.*, 1896, **32**, 101; *Amer. Chem. J.*, 1897, **19**, 243; *Chem. Soc. Abs.*, 1897, **72** (1), 389.

[d] *Ind. Eng. Chem.*, 1924, **16**, 263.

[e] *J.C.S.*, 1897, **71**, 440; *ibid.*, 1898, **73**, 905, 920.

[f] *Ber.*, 1897, **30**, 975; *Chem. Soc. Abs.*, 1897, **72** (1), 329.

[g] Redwood, "A Treatise on Petroleum," Charles Griffin and Co., Ltd., London, 1913, 1, 242.

[h] *Proc. Am. Acad. Arts Sci.*, 1891, **27**, 56; *ibid.*, 1898, **34**, 92.

[i] *Proc. Am. Acad. Arts Sci.*, 1895, **31**, 10; *Amer. Chem. J.*, 1895, **17**, 713; *Chem. Soc. Abs.*, 1896, **70** (1), 269.

[j] *Bull. soc. chim. belg.*, 1921, **30**, 8; *Chem. Abs.*, 1922, **16**, 1389.

[k] *J.C.S.*, 1863, **15**, 419.

[l] *J.C.S.*, 1879, **35**, 296.

[m] *J.A.C.S.*, 1911, **33**, 520.

[n] *Bull. soc. chim.*, 1884, **41**, 161; *Chem. Soc. Abs.*, 1884, **46**, 1107.

but not completely frozen. In all probability a small amount of a heptane was present which could not be separated by fractional distillation, but fractional crystallization resulted in the separation of pure cyclohexane[98] boiling at 80.85° C. This hydrocarbon has also been isolated from certain fractions (boiling about 80° C.) of Mid-Continent crude petroleum.[99] Bruun and Hicks-Bruun[100] later isolated and determined methylcyclohexane (boiling point, 100.8° C.) in this petroleum.

A number of cyclohexane homologues have been identified in fractions of various crudes. These include methylcyclohexane,[101] 1,2- and 1,3-dimethylcyclohexanes,[102] 1,2,4-trimethylcyclohexane[103] and two isomeric decanaphthenes[104] (probably dimethylethylcyclohexanes). Skowronski[105] made a study of the lower cyclohexanes in a petroleum from Tustanowic (Galicia). The crude petroleum was carefully fractionated and the fractions were purified with cold fuming sulphuric acid. The cyclohexane hydrocarbons present in the residual oil were then oxidized, by heating with iodine, to the corresponding benzene hydrocarbons which were identified as their bromo-derivatives. Besides the above cyclohexane homologues, the presence of 1,4-dimethylcyclohexane was definitely established. Octa-, nona- and decanaphthenes have been found in Japanese petroleums.[106] Bicyclic naphthenes, chiefly derivatives of hydrogenated naphthalenes, have been found in various gasolines, for example the decahydronaphthalene isolated by Ross and Leather[107] from Borneo petroleum. The bicyclic hydrocarbons $C_{10}H_{18}$ and $C_{13}H_{24}$ isolated by Coates[108] from the Jennings, La., crude were probably dicyclopentyl and its methylated derivatives.

The actual proportions of aromatic hydrocarbons in most petroleums are usually relatively small.[109] On account of their greater ease of identification (since they can be readily converted to characteristic crystalline derivatives) the aromatic hydrocarbons have received much more attention than the naphthenes. In addition to the simple benzene homologues, more complicated polynuclear aromatic hydrocarbons (including naphthalene and its homologues) have also been identified.

Benzene and toluene are present in many crudes, notably in the gasoline from Koetei (Borneo) petroleum. Mabery[110] identified m- and p-xylenes in Ohio and Canadian crude petroleum. Tausz[111] showed that o-xylene and ethylbenzene also occur in many petroleums. According to Tausz, the relative proportions of the three xylenes and ethylbenzene (calculated on the total C_8 aromatic hydrocarbon content) in various petroleums are as given in Table 8.

Investigations of the aromatic hydrocarbons of Burma petroleum have been made by Mulany and Watson[112] and of Byoritsu (Formosa) crude by Kurihara.[113] The percentages of benzene, toluene, and xylenes in the fraction of the Byoritsu crude distilling up to 155° C. were 3.1 per cent, 20.2 per cent and 20.9 per cent of the distillate or 1 per cent, 8 per cent and 8 per cent of the crude, respectively. Besides benzene and toluene, m- and p-xylenes, mesitylene, and naphthalene were definitely identified in this crude.

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[98] Young and Fortey, *J.C.S.*, 1899, **75**, 873.

[99] Bruun and Hicks-Bruun, *Bur. Standards J. Research*, 1931, **7**, 607; *Chem. Abs.*, 1932, **26**, 286.

[100] *Bur. Stand. J. Res.*, 1932, **8**, 525; *Chem. Abs.*, 1932, **26**, 3655. *Cf.* Tongberg and Fenske, *Ind. Eng. Chem.*, 1932, **24**, 814.

[101] Mabery and Hudson, *Amer. Chem. J.*, 1901, **25**, 253; *J.S.C.I.*, 1901, **20**, 568. Mabery and Sieplein, *Amer. Chem. J.*, 1901, **25**, 286; *Chem. Soc. Abs.*, 1901, **80** (1), 306. Mabery and Takano, *Amer. Chem. J.*, 1901, **25**, 301; *J.S.C.I.*, 1901, **20**, 569. Young, *J.C.S.*, 1898, **73**, 906.

[102] Markownikow and Oglobin, *J. Russ. Phys. Chem. Soc.*, 1883, **15**, 332. Mabery and Hudson, *loc. cit.*, Mabery and Sieplein, *loc. cit.*

[103] Markownikow and Oglobin, *J. Russ. Phys. Chem. Soc.*, 1883, **15**, 331; *Ber.*, 1883, **16**, 1877.

[104] Markownikow and Oglobin, *loc. cit.*; Zubkow, *J. Russ. Phys. Chem. Soc.*, 1893, **25**, 383; *Chem. Soc. Abs.*, 1894, **66** (1), 160.

[105] Metan, 1918, 61, 73, 86, 97, 109; *Chem. Abs.*, 1920, **14**, 3523.

[106] Kobayashi, *J. Soc. Chem. Ind. Japan*, 1932, **35**, Suppl. binding 426; *Chem. Abs.*, 1933, **27**, 183.

[107] *Analyst*, 1906, 31, 284; *Chem. Soc. Abs.*, 1906, **90** (2), 815.

[108] *J.A.C.S.*, 1906, **28**, 384; see Schmidt and Sigwart, *Ber.*, 1912, **45**, 1779.

[109] See Brooks and Humphrey, *J.A.C.S.*, 1916, **38**, 393.

[110] *Amer. Chem. J.*, 1896, **18**, 43; *Chem. Soc. Abs.*, 1896, **70** (1), 270; *Proc. Amer. Acad.*, 1895-6, **31**, 60.

[111] *Z. angew. Chem.*, 1919, **32** (1), 361; *Chem. Abs.*, 1920, **14**, 2258.

[112] *J.S.C.I.*, 1924, **43**, 310T.

TABLE 8.—*Per Cent of Total C_8 Aromatic Content.*

Petroleum	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
Rumania	26	24	42	17
Pennsylvania	13	36	47	4
California	16	20	56	8
Hannover	13	43	40	4
Borneo	16	10	62	12

Bruun, Leslie and Schicktanz[114] observed that all the fractions of an Oklahoma crude oil boiling from 90° to 112° C. contained toluene. The greatest concentration of this aromatic hydrocarbon was found in the fraction boiling between 107° and 108° C. Estimation of toluene by converting it to 2,4-dinitrotoluene indicated that it was present in the crude oil to the extent of 0.33 per cent. From this same petroleum were later isolated the three xylenes,[115] ethylbenzene[116] (boiling at 136.05° C.), mesitylene, pseudocumene, and hemimellitene.[117] A cyclic hydrocarbon, $C_{10}H_{16}$, melting at 268° C., to which was given the name adamantane, was separated from a Hodonin (Moravian) petroleum by Landa and Macháček.[118] According to Birch and Norris,[119] mesitylene and pseudocumene are probably the commonest aromatic constituents of liquid petroleums and usually occur together.

The hydrocarbons which have been isolated by investigators at the U. S. Bureau of Standards from a single sample of crude oil obtained from well No. 6 of the South Ponca field, Kay County, Oklahoma,[120] a typical Mid-Continent crude, are shown in Table 9.[121]

KEROSENE

The kerosenes obtained from American crudes follow the same general trend, as regards chemical characteristics, as gasolines. Eastern kerosenes are more paraffinic and those from California more aromatic. The identification of definite hydrocarbons, and even of definite classes of hydrocarbons, in kerosene fractions is a matter of great difficulty. As has been previously mentioned, because of the ease with which aromatic hydrocarbons may be segregated with liquid sulphur dioxide and because of their ready conversion into easily identifiable derivatives, our knowledge of the aromatic content of kerosenes is much more extensive than that of the other classes of hydrocarbons. In the large-scale refining of kerosenes by the Edeleanu process, which makes use of the preferential solvent action of liquid sulphur dioxide, the aromatic hydrocarbons are for the most part removed from the bulk of the kerosene. The sulphur dioxide extract is thus a valuable source of aromatic hydrocarbons offering commercial possibilities.

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[113] *J. Chem. Ind. (Japan)*, 1924, 27, 831; *Chem. Abs.*, 1925, 19, 574.

[114] *Bur. Stand. J. Res.*, 1931, 6, 363; *Chem. Abs.*, 1931, 25, 2551.

[115] White and Rose, *Bur. Stand. J. Res.*, 1932, 9, 711; *Chem. Abs.*, 1933, 27, 1491.

[116] White and Rose, *Bur. Stand. J. Res.*, 1933, 10, 639; *Chem. Abs.*, 1933, 27, 4062.

[117] Mair and Schicktanz, *Bur. Stand. J. Res.*, 1933, 11, 665.

[118] *Coll. Czechoslov. Chem. Comm.*, 1933, 5, 1; *Chem. Abs.*, 1933, 27, 2792.

[119] *J.C.S.*, 1926, 2545.

[120] Characteristics of this have been described by Washburn, Bruun and Hicks, *Bur. Stand. J. Res.*, 1929, 2, 467.

[121] This tabulation was made by Washburn, *Ind. Eng. Chem.*, 1933, 25, 891.

TABLE 9.—*Hydrocarbons Isolated from Oklahoma Petroleum.*

Hydrocarbon	Boiling Point ° C.	Per Cent in Crude Oil	Reference
	Paraffin		
Ethane	—	[a]	
Propane	—	[a]	
Butane	—	[a]	
Pentane (two isomers)	—	[a]	
n-Hexane	68.7°	0.5	[b]
2,3-Dimethylbutane	58°–58.3°		[c]
2-Methylpentane	60.4°–60.6°	0.3	[c]
3-Methylpentane	63.2°–63.3°		[c]
n-Heptane	98.4°	0.9	[d]
2,2-Dimethylpentane	79.5°	<0.03	[e]
2-Methylhexane	89.67°	0.25	[f]
3-Methylhexane	—	[r]	
n-Octane	125.4°	1.	[g]
2-Methylheptane	117.2°	0.16	[h]
n-Nonane	—	1.	[j]
n-Decane	174.0°	0.8	[k]
	Naphthene		
Cyclopentane	—	[a]	
Methylcyclopentane	—	0.2	[l]
Cyclohexane	80.8°	0.3	[m]
Methylcyclohexane	100.8°	0.3	[d]
1,1-Dimethylcyclopentane	87.5°	<0.03	[f]
Nonanaphthene	—	[r]	
	Aromatic		
Benzene	80.1°	0.08	[b]
Toluene	—	0.3	[n]
o-Xylene	144.4°	0.12	[o]
m-Xylene	139.15°	0.12	[o]
p-Xylene	138.4°	0.04	[o]
Ethylbenzene	136.05°	0.03	[p]
Hemimellitene			[q]
Pseudocumene			[q]
Mesitylene			[q]

[a] Not determined.
[b] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1931, 6, 869.
[c] Bruun and Hicks-Bruun, *ibid.*, 1930, 5, 933.
[d] Hicks-Bruun and Bruun, *ibid.*, 1932, 8, 525.
[e] Bruun and Hicks-Bruun, *ibid.*, 1932, 9, 53.
[f] Bruun and Hicks-Bruun, *ibid.*, 1933, 10, 465.
[g] Leslie and Schicktanz, *ibid.*, 1931, 6, 377.
[h] Leslie, *ibid.*, 1933, 10, 609.
[j] White and Rose, *ibid.*, 1931, 7, 907.
[k] Bruun and Hicks-Bruun, *ibid.*, 1932, 8, 583.
[l] Hicks-Bruun and Bruun, *ibid.*, 1931, 7, 799.
[m] Bruun and Hicks-Bruun, *ibid.*, 1931, 7, 607.
[n] Bruun, Leslie and Schicktanz, *ibid.*, 1931, 6, 363.
[o] White and Rose, *ibid.*, 1931, 9, 711.
[p] White and Rose, *ibid.*, 1933, 10, 639.
[q] Mair and Schicktanz, *ibid.*, 1933, 11, 665.
[r] Determinations in progress, to be reported.

The sulphuric acid method of refining petroleum distillates also tends to remove the aromatic hydrocarbons in the form of the so-called "acid sludge." The aromatic hydrocarbons present in the acid sludge obtained by treating Persian kerosene with fuming sulphuric acid (20% SO_3) have been investigated by Birch and Norris.[122] The following hydrocarbons were definitely identified by the preparation of crystalline derivatives: toluene, m- and p-xylenes, mesitylene, pseudocumene, hemimellitene, p-ethyltoluene, an ethylxylene, a dimethylnaphthalene, and some indication of a trimethylnaphthalene.

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[122] *J.C.S.*, 1926, 2545.

According to Mulany and Watson,[123] p-cymene is the most important aromatic constituent of Burma kerosene. The aromatic hydrocarbons present in Burma crude have also been studied by Carpenter[124] who found indications of the presence of hydrocarbons up to pentaethylbenzene (boiling point, 277° C.).

Bicyclic hydrocarbons of the aromatic and hydroaromatic type occur in many kerosenes. Mabery[125] isolated naphthalene from a fraction (boiling point, 220°-222° C.) of a California petroleum. The mono- and dimethyl derivatives of naphthalene were found by Jones and Wootton[126] in a Borneo petroleum, which contained 6 to 7 per cent of naphthalene hydrocarbons. Naphthalene, 2-methylnaphthalene and 2,6-dimethylnaphthalene have been isolated from the kerosene acid sludge of a Formosa crude.[127] Hydrocarbons of the formulas $C_{12}H_{18}$, $C_{14}H_{20}$, $C_{13}H_{18}$, and $C_{14}H_{18}$ were isolated by Wagner[128] from the sulphur dioxide extract of an Oklahoma kerosene. These were considered to be partly hydrogenated substituted naphthalenes. The part of the kerosene insoluble in liquid sulphur dioxide was said to be practically unaffected by sulphuric acid (specific gravity, 1.84) and consisted essentially of members of the cyclohexane series.

Of the non-aromatic hydrocarbons of kerosene fractions of petroleum, comparatively little definite information is available. There is little doubt, however, that most kerosenes consist very largely of paraffins and cycloparaffins (cyclohexane and cyclopentane homologues), but the separation of pure chemical individuals of these series from kerosene fractions is almost impossible by ordinary fractionation methods. Incidentally, the influence of various hydrocarbons, especially the aromatics and olefins, on the light intensity of kerosenes is a subject of controversy.[129]

HIGHER FRACTIONS OF PETROLEUM

Knowledge of the chemical nature of the high-boiling hydrocarbon constituents of petroleum is also meager. This is not surprising in view of the extreme complexity of such hydrocarbon mixtures and the difficulty of distilling them without decomposition. For these reasons fundamental research on the chemical nature of the higher petroleum hydrocarbons has made but little progress despite much painstaking effort. Various attempts have been made to utilize selective solvent action for concentrating the hydrocarbons into fractions of particular types. Though theoretically this method is excellent, since it avoids conditions where decomposition and molecular rearrangements are likely to occur, it has not led to any definite results in practice. However, Mabery[130] employed, with some success, a mixture of ether and ethyl alcohol for effecting some separation of various high-boiling petroleum fractions.

A general characteristic of petroleum hydrocarbons as a class is that, though the lower-boiling fractions (gasolines and kerosenes) approximate the formulas C_nH_{2n+2} (paraffins) and C_nH_{2n} (naphthenes), the higher-boiling fractions consist of hydrocarbons much more deficient in hydrogen. Hydrocarbons having the approximate general formulas C_nH_{2n-12} to even C_nH_{2n-20} have been found in the highest fractions of some petroleums. The higher-boiling fractions from even those typically paraffinic crudes which yield gasolines and kerosenes consisting largely of paraffin hydrocarbons contain relatively small amounts of saturated hydrocarbons. Thus, the paraffin wax content of light lubricating oils seldom exceeds 6 per cent. No paraffins, other than those in the wax, have been identified in the lubricating fractions. Paraffin wax is produced commercially on a large scale by chilling light lubricant fractions of petroleum.[131] The commercial product ordinarily melts between 48° and 62° C. and consists largely of a mixture of hydrocarbons of 23 to 28 carbon atoms per molecule. The principal constituents of paraffin wax are the normal paraffin hydrocarbons, but in addition to these straight-chain compounds, other types of hydrocarbons, probably branched-chain paraffins or isoparaffins (rather than unsaturated or cyclic compounds) are present.[132] Buchler and Graves [133] found paraffins ranging from $C_{18}H_{38}$ to $C_{43}H_{88}$ in paraffin wax, slop wax, petrolatum, and rod wax. Besides the freely crystallizing varieties of paraffin wax, there are also so-called amorphous waxes, which are very troublesome to refiners. These amorphous waxes are regarded by some [134] as ordinary paraffins whose crystallization has been inhibited by the presence of colloidal impurities. Though the real nature of amorphous wax has not yet been elucidated, some evidence has been advanced to show that it probably consists of a mixture of branched-chain paraffins.[135] Nametkin and Nifontova,[136] from a study of the nitro-derivatives of a Grozny and an American paraffin wax, concluded that about 25 to 30 per cent of isoparaffins were present. The presence of naphthenic or unsaturated hydrocarbons in both crystalline and amorphous waxes is not definitely disproved though somewhat doubtful, in view of the evidence.

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[123] *J.S.C.I.*, 1924, 43, 310T.

[124] *J. Inst. Pet. Tech.*, 1926, 12, 518; *Chem. Abs.*, 1927, 21, 1702.

[125] *J.S.C.I.*, 1900, 19, 502.

[126] *J.C.S.*, 1907, 91, 1146.

[127] Tasaki and Yamamoto, *J. Chem. Ind. (Japan)*, 1931, 34, 247; *Chem. Abs.*, 1932, 26, 288.

[128] *Ind. Eng. Chem.*, 1924, 16, 135.

[129] Dănăilă, Stoenescu, and Dinescu, *Petroleum Z.*, 1930, 26, 47; *Chem. Abs.*, 1930, 24, 2588; *Petroleum Z.*, 1932, 28 (17), 1; *Chem. Abs.*, 1932, 26, 4704; Grote and Hundsdörfer, *Petroleum Z.*, 1932, 28, 9; *Chem. Abs.*, 1932, 26, 5745; Dănăilă, *Petroleum Z.*, 1933, 29 (7), 1; *Chem. Abs.*, 1933, 27, 3595; see also Chapter 50.

[130] *Ind. Eng. Chem.*, 1923, 15, 1233.

Ceresin, a purified form of ozokerite (mineral wax), presumably consists also of a mixture of paraffin hydrocarbons, probably mainly isoparaffins, of somewhat higher average molecular weight than those of paraffin wax. Marcusson [137] examined the distillation products of ceresin and found saturated hydrocarbons and olefins of low molecular weight but obtained no evidence of the presence of naphthenes. Shale oil is also a source of paraffin wax.[138]

The so-called vaseline (petrolatum or petroleum jelly), which is made by careful filtration of certain residual oils through decolorizing earth, possesses the colloidal characteristics of a gel. Mabery [139] found that the commercial product consisted of heavy oils which form the high-boiling portion of Pennsylvania petroleum, hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-4}, together with solid paraffin hydrocarbons.

Little is known about the constitution of the hydrocarbons of the lubricating oil range. It is almost certain that normal or straight-chain paraffin hydrocarbons are absent, or present only in small amounts. Kyropoulos [140] considered the typical lubricating fractions from Pennsylvania crude oils to consist largely of isoparaffins, and Davis and McAllister[140a] believe that this type of oil consists essentially of a combination of naphthene rings and paraffin chains. The simple naphthenes, apparently homologues of cyclohexane and cyclopentane, together with polynaphthenes (fully saturated polycyclic hydrocarbons), have been reported by Seyer and Huggett[141] to be present in a lubricating fraction of Peruvian petroleum. Mabery,[142] in a comprehensive study of the lubricating fractions of various crudes, did not find the simple naphthenes in any of the oils examined. He concluded that the most highly saturated hydrocarbons in American petroleum which exhibit lubricating properties belong to the series C_nH_{2n-2}, and the hydrocarbons comprising the main bulk of the light and medium-heavy lubricants are of the series C_nH_{2n-4}. The heavier grades of lubricants conform to the formula C_nH_{2n-8}, but hydrocarbons even more deficient in hydrogen (series C_nH_{2n-10}, C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16}, and C_nH_{2n-18}) were also encountered. Charitschkoff[143] found a hydrocarbon, $C_{19}H_{38}$, and several of the series C_nH_{2n-2} ($C_{10}H_{36}$, $C_{21}H_{40}$, $C_{22}H_{42}$, $C_{24}H_{46}$ and $C_{35}H_{68}$) in Groszny petroleum. Much of what has been written concerning the chemical structures of these hydrocarbons is purely conjectural. It is significant, however, that in the examination of lubricating fractions from various crudes, Mabery found fractions of the same general formula (e.g., C_nH_{2n-8}) which differed widely in specific gravity, a fact which may be ascribed to paraffin-chains attached to more or less complex ring structures of aromatic and naphthenic character.

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[131] Following this chilling process and separation of the oil and wax by pressing, the wax is generally submitted to a "sweating" operation in which the major portion of the entrained oil is removed. Allibone (British Patent 358,668, 1930; assigned to Burmah Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 11) has suggested that following the sweating operation the wax be distilled at low pressures (2 to 10 mm.) in order to produce products of more clearly defined melting points. For a method of determining the quantity of wax in petroleum products, see Tormey, *Analyst,* 1931, **20** (6), 15; *Brit. Chem. Abs.* **B**, 1932, 376.

[132] Ferris, Cowles and Henderson, *Ind. Eng. Chem.,* 1929, **21**, 1090; *ibid.,* 1931, **23**, 681.

[133] *Ind. Eng. Chem.,* 1927, **19**, 718.

[134] See Gruse, "Petroleum and its Products," McGraw-Hill Book Co., Inc., New York, 1928, 280; *cf.* Carpenter, *J. Inst. Pet. Tech.,* 1926, **12**, 288; *cf.* also Myers and Stegeman, *Ind. Eng. Chem.,* 1928, **20**, 638.

[135] Marcusson, *Chem. Ztg.,* 1915, **39**, 581, 613; *Chem. Abs.,* 1915, **9**, 2813.

[136] *J. Appl. Chem., Russ.,* 1933, **6**, 248; *Brit. Chem. Abs.* **B**, 1933, 692.

[137] *Loc. cit.*

[138] The composition of such a wax is discussed by Beilby, *J.C.S.,* 1883, **43**, 388.

[139] *Amer. Chem. J.,* 1905, **33**, 251; *Chem. Soc. Abs.,* 1905, **88** (1), 313.

[140] *Z. phys. Chem.,* 1929, **144**, 22; *Brit. Chem. Abs.* **B**, 1929, 931.

Not only the specific gravity, but the viscosity of hydrocarbons as well, is dependent on the chemical structure. Hugel[144] observed that, for hydrocarbons of the same molecular weight, the viscosity of cyclic hydrocarbons is greater than that of paraffins. Introduction of side chains, as well as unsaturation, had little effect on the viscosity of acyclic hydrocarbons. With cyclic hydrocarbons, however, the introduction of side chains, particularly methyl groups, had a specific effect though not always in the same direction. The viscosity of unsaturated compounds was increased by saturation.

Though it has often been suggested that unsaturated hydrocarbons are present in lubricating fractions,[145] it is more probable that the main constituents of these oils are polynuclear naphthenes, some of which, on account of their ability to undergo nuclear fission under certain conditions, simulate the reactions of unsaturated compounds.

NON-HYDROCARBON CONSTITUENTS OF PETROLEUM

Crude petroleums often contain appreciable proportions of organic substances other than hydrocarbons. Organic carboxylic acids are present in a number of crudes and are discussed in Chapter 48 under the generic designation, naphthenic acids. Phenolic compounds have been found in some crudes.[146] The asphaltic constituents of crude petroleum consist essentially of highly condensed oxygenated compounds. The sulphur-containing compounds comprise not only hydrogen sulphide and its organic derivatives (such as mercaptans and disulphides) but also more complicated sulphur compounds, including thiophene and its derivatives.[147] Some crudes even contain relatively large amounts of elemental sulphur. Organic bases, which include complex nitrogen compounds, also occur in petroleum. Interest in these nitrogen compounds has been revived, largely as a result of a series of investigations of their properties and constitution. A detailed account of these substances is to be found in Chapter 35.

[140a] *Ind. Eng. Chem.*, 1930, **22**, 1326.

[141] *Trans. Roy. Soc. Canada*, 1926, **20**, 193; *Chem. Abs.*, 1926, **20**, 2407.

[142] *Ind. Eng. Chem.*, 1923, **15**, 1233; *ibid.*, 1927, **19**, 526.

[143] *Chem. Rev. Fett- u. Harz-Ind.*, 1903, **10**, 251, 281; *ibid.*, 1904, **11**, 9; *Chem. Zentr.*, 1904, **1**, 409. See Mabery, *Ind. Eng. Chem.*, 1923, **15**, 1233. The name "Charitschkoff" is transliterated in various ways, for example, Kharichkov (preferred by *Chem. Abs.*); Charitschkoff (used by *Chem. Zentr.* and *J.S.C.I.*); Charichkoff, and Charisckov.

[144] *Chim. et Ind.*, 1931, **26**, 1282; *Brit. Chem. Abs.* **A**, 1932, 116.

[145] See Dunstan and Thole, *Chem. Met. Eng.*, 1923, **28**, 300; *Chem. Abs.*, 1923, **17**, 1289; Stäger, *Helv. Chim. Acta*, 1923, **6**, 893; *Chem. Abs.*, 1924, **18**, 164; Wilson and Allibone, *J. Inst. Pet. Tech.*, 1925, **11**, 177; *Chem. Abs.*, 1925, **19**, 2410.

[146] See Story and Snow, *Ind. Eng. Chem.*, 1928, **20**, 359. Phenols in shale oil have been determined by Lazar, *Chem.-Ztg.*, 1921, **45**, 197; Waterman, deJong and Tulleners, *J. Inst. Pet. Tech.*, 1932, **18**. 183. The separation of phenols from hydrocarbons is described by I. G. Farbenindustrie A.-G. (French Patent 739,742, 1932; *Chem. Abs.*, 1933, **27**, 2293), and by Masters (U. S. Patent 1,817,444, Aug. 4, 1931; assigned to Elko Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 218).

The presence of inorganic matter in petroleum is of interest in connection with various theories of its origin.[148] The percentage of ash obtained by ignition of various crude petroleums varies widely but appears to be highest with the more asphaltic crudes, such as those of Mexico. Analyses of the ash of crudes have been made by Ramsay,[149] Thomas,[150] and Shirey.[151] Both vanadium and nickel occur in petroleum ash. Although nickel apparently occurs to some extent in the ash of all crudes, vanadium appears to associate itself more strictly with those of asphaltic nature. A vanadium pentoxide content of as high as 45 per cent has been reported in the ash from a Venezuela petroleum.[152] Several processes have been developed for the extraction of vanadium from petroleum ash.[153] Table 10 shows the vanadium and nickel content of the ash of various asphaltic crude petroleums:

TABLE 10.—*Vanadium and Nickel Content of Petroleum Ash.*

Source	Base	Per Cent of Ash	
		V_2O_5	NiO
Persia	1.17 asphaltum	5.03	2.70
Oklahoma	asphalt	22.14	5.89
Kansas	——	0.44	0.57
Texas Panhandle	——	1.43	1.52
Mid-Continent	——	trace	0.52
Wyoming	——	trace	0.33

The occurrence of vanadium in petroleum ash has been discussed also by Porter [154] and by DeGolyer.[155]

PURE HYDROCARBONS FROM PETROLEUM

The separation of pure hydrocarbons from petroleum is the initial stage in the chemical utilization of such hydrocarbons. Since, in general, synthetic chemicals must conform to rigid standards of purity and chemical homogeneity, it is ordinarily essential to start with pure compounds as raw materials. Although industrial distillation apparatus when specially designed for a particular purpose is much more efficient than laboratory equipment, yet the large-scale separation of individual hydrocarbons above heptane in the paraffin series, or above cyclohexane in the cycloparaffin series, in a degree of purity comparable with that of toluene for synthetic purposes, is a matter of great difficulty by distillation alone.[155a]

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[147] Sulphur compounds are discussed in Chapter 19.

[148] Ramsay, *J. Inst. Pet. Tech.*, 1924, 10, 87. Hackford, *ibid.*, 1922, 8, 193; *Chem. Abs.*, 1922, 16, 2403; Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, 1932, 280.

[149] Ramsay, *J. Inst. Pet. Tech.*, 1924, 10, 87.

[150] Thomas, *J. Inst. Pet. Tech.*, 1924, 10, 216; *Chem. Abs.*, 1924, 18, 2241.

[151] *Ind. Eng. Chem.*, 1931, 23, 1151.

[152] Broz, *Arh. hem. farm.*, 1930, 4, 89 (90-1 German); *Chem. Abs.*, 1930, 24, 3348.

[153] Baldeschwieler, U. S. Patent 1,563,061, Nov. 24, 1925; *Chem. Abs.*, 1926, 20, 502. Oberle, U. S. Patent 1,570,170, Jan. 19, 1926; *Chem. Abs.*, 1926, 20, 817.

[154] *Mining and Met.*, 1924, 5, 133; *Chem. Abs.*, 1924, 18, 2307.

[155] *Econ. Geol.*, 1924, 19, 550; *Chem. Abs.*, 1924, 18, 3582.

As has been indicated previously, it is a matter of comparative ease, both on a large scale and in the laboratory,[156] to isolate the lower paraffin hydrocarbons (methane, ethane, propane, and the two butanes) from natural gas. This facility is to be attributed to the relatively great differences in the boiling points of these hydrocarbons, or in other words, to the great differences in their vapor pressures at any particular temperature. The difference between the boiling points of methane and propane at atmospheric pressure is fully 70° C. Propane boils 45° C. higher than ethane, and n-butane about 44° C. above propane. With increasing molecular weight, however, the differences between the vapor pressures of the members of the series decreases, so that increasing difficulty is experienced in effecting a separation. Moreover, the existence of an increasing number of isomers,[157] as has been mentioned previously, further complicates the matter.

Pure paraffin hydrocarbons from methane to butane (also isobutane) are readily obtained by careful pressure-fractionation of wet natural gas. The principles of such natural-gas fractionation have been described by Beall [158] and need not be discussed here. Relatively pure propane and a mixture of the two butanes, as previously stated, are now available in liquid form in cylinders for fuel purposes. The isolation of pure methane from coal-distillation gases may also be readily effected but in this case the problem is complicated by the presence of gaseous olefins, particularly ethylene. Adsorption on charcoal can be applied for further purification—for example, for separating higher hydrocarbons from methane.[158a]

Of the three isomeric pentanes, all of which are present in natural-gas gasoline, tetramethylmethane is the least abundant. Nevertheless, it is not a very difficult matter to obtain it pure by careful fractionation and in 1925 several hundred gallons of the hydrocarbon (boiling point, 9.5° C.) were isolated by this method.[159] Similarly, the recovery of a substantially pure mixture of n-pentane (boiling point, 36° C.) and isopentane (boiling point, 28° C.) was effected by fractional distillation. It is not quite as easy to obtain n-pentane and isopentane separately but with efficient modern equipment the large-scale separation of the pure isomers has been successfully accomplished.

No attempt has been made to produce paraffins higher than n-pentane on a large scale, but diisopropyl (boiling point, 58° C.) and dimethylpropylmethane

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[155a] Piper, Chibnall, Hopkins, Pollard, Smith and Williams (*Biochem. J.*, 1931, 25, 2072; *Chem. Abs.*, 1932, 26, 2696) synthesized some highly purified paraffins from $C_{24}H_{50}$ to $C_{36}H_{74}$ and offered suggestions to aid in the fractionation and identification of the paraffins of petroleum.

[156] Separation of hydrocarbons by precise fractional-distillation analysis is discussed in Chapter 49; see Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 177.

[157] The following figures (Henze and Blair, *J.A.C.S.*, 1931, 53, 3077) show how rapidly the number of isomeric paraffin hydrocarbons increases with increasing carbon content:

Carbon Atoms	*Isomers*	*Carbon Atoms*	*Isomers*
1	1	7	9
2	1	8	18
3	1	10	75
4	2	12	355
5	3	14	1858
6	5	16	10359

No simple or direct relationship appears to exist between the number of isomeric paraffin hydrocarbons and the number of carbon atoms in the molecule.

Blair and Henze made calculations also for the number of non-stereoisomeric and stereoisomeric paraffin hydrocarbons (*J.A.C.S.*, 1932, 54, 1538), the number of structurally isomeric alcohols of the methanol series (*J.A.C.S.*, 1931, 53, 3042), the stereo- and non-stereoisomeric monosubstitution products of the paraffins (*J.A.C.S.*, 1932, 54, 1098), and the number of isomeric hydrocarbons of the acetylene series (Coffman, Blair and Henze, *J.A.C.S.*, 1933, 55, 252). Perry (*J.A.C.S.*, 1932, 54, 2918) calculated the number of certain homologues of methane and methyl alcohol.

[158] *Refiner*, 1931, 10 (1), 110; *Chem. Abs.*, 1931, 25, 1360. For fractional liquefaction of natural gas, see Claude and Jordan, U. S. Patent 1,497,546, June 10, 1924; *Chem. Abs.*, 1924, 18, 2421; Dumars, U. S. Patent 1,747,761, Feb. 18, 1930; *Chem. Abs.*, 1930, 24, 1726.

[158a] Storch and Golden, *J.A.C.S.*, 1932, 54, 4662.

[159] Ayres, *Ind. Eng. Chem.*, 1929, 21, 899.

(boiling point, 62° C.) could probably be isolated in a relatively pure condition if a demand for these hydrocarbons were assured.

Investigations have shown that normal paraffins may be separated from the more reactive branched-chain isomers with certain chemical reagents, such as chlorosulphonic acid.[160] Although this is undoubtedly of value in the laboratory, its applicability to large-scale work is doubtful. High homologues of methane can be purified by various procedures, for example, by steam distillation;[161] by fractional distillation in high vacuum, which has been used for separating mixtures of eicosane and triacontane, and tetracosane and triacontane;[162] or by crystallization from liquid hydrocarbons, the method used by Leslie[163] for the isolation of 2-methylheptane from petroleum.

The isolation of simple mononaphthenes in a state of high purity has never been attempted on a large scale, but comparatively pure cyclohexane, cyclopentane and their immediate homologues have been obtained in the laboratory from various crude petroleums. Since, however, the few industrially valuable derivatives of cyclohexane can readily be prepared from the corresponding benzene derivatives, it is somewhat unlikely that the mononaphthenes of petroleum, containing a six-membered carbon ring system, will be utilized as raw materials for chemical synthesis. The aromatization of such cyclohexanes can be effected by thermal dehydrogenation.

The aromatic hydrocarbons present in gasoline and kerosene fractions of petroleum are of considerable interest from the standpoint of chemical synthesis. Although coal tar is a source of aromatic substances, the benzene homologues found in such tars have a tendency to conform to certain definite configurations.[163a] Thus, of the benzene homologues present in coal tar, the m-disubstituted and the 1,3,5-trisubstituted types predominate. It is therefore more than probable that aromatic hydrocarbons of petroleum will be used as a source of benzene homologues which do not occur, or which are present only in small proportions, in coal tar. Bicyclic and polycyclic aromatic derivatives also occur in petroleum but are of less interest at present from a technical point of view since they are abundant in coal tar.

For the separation of aromatic hydrocarbons from petroleum distillates, fractionation is usually inadequate if pure products are desired. However, fractionation of some gasolines rich in aromatics yields fairly pure benzene and toluene. To isolate the higher aromatics it is advantageous to adopt a method of partially concentrating the aromatic hydrocarbons from the paraffins and naphthenes. On account of the greater chemical reactivity of the aromatic hydrocarbons as a class, several such methods are known. Selective solvent action, for example, can be employed.[163b] Both sulphuric acid and liquid sulphur dioxide exert a selective solvent action on the aromatic hydrocarbons of gasolines and kerosenes. The latter solvent is used in the well-known Edeleanu process[164] for the removal of aromatic hydrocarbons from kerosene distillates. Edeleanu's investigations were started with a Rumanian kerosene distillate containing 25 per cent of aromatics, the presence of which caused the kerosene to burn with a sooty flame. The removal of this large proportion of aromatic hydrocarbons required fuming sulphuric acid and entailed high refining losses. It was found that liquid sulphur dioxide at —10° C. extracted the aromatics with smaller refining losses. Two liquid layers are formed, the upper (having a specific gravity of 0.9 to 1.0) consisting of the refined oil saturated with sulphur dioxide, and the lower (with a specific gravity of 1.3 to 1.4), a solution of the extract in sulphur dioxide. The two layers are easily separated and the sulphur dioxide can be evaporated at a temperature low enough to avoid any considerable loss of hydrocarbons. This Edeleanu extract is a possible fruitful source of aromatic hydrocarbons for chemical synthesis.

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[160] Shepard, Henne and Midgley, *J.A.C.S.*, 1931, **53**, 1948.

[161] Abderhalden, *Rev. pétrolifère*, 1932, 905; *Chim. et ind.*, 1932, **29**, 309; *Chem. Abs.*, 1933, **27**, 2792.

[162] Gilchrist and Karlik, *J.C.S.*, 1932, 1992.

[163] *Bur. Stand. J. Res.*, 1933, **10**, 609; *Chem. Abs.*, 1933, **27**, 4062; *cf.* I. G. Farbenindustrie A.-G., British Patent 389,113, 1933; *Chem. Abs.*, 1933, **27**, 4666.

[163a] The composition of coal tar is discussed by Fischer ("The Conversion of Coal into Oils," translated by Lessing, D. Van Nostrand Co., Inc., New York, **1925**, 38) and Allen ("Commercial Organic Analysis," P. Blakiston's Sons and Co., Philadelphia).

[163b] See Hunter and Nash, "A Study of the Principles of Solvent Extraction Processes for the Refining of Oil," World Petroleum Congress, London, July 1933.

[164] See Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, **1932**, 475. Kalichevsky and Stagner, "The Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, **1933**, 220. Edeleanu, *J. Inst. Pet. Tech.*, 1932, **18**, 900; U. S. Patent 1,776,752, Sept. 23, 1930; *Chem. Abs.*, 1930, **24**, 5475; U. S. Patent 1,776,753, Sept. 23, 1930; *Chem. Abs.*, 1930, **24**, 5478; German Patent 571,712, 1933; *Chem. Abs.*, 1933, **27**, 4388; all patents

Sulphuric acid exerts a preferential solvent action for aromatic hydrocarbons and many sulphur compounds. Thus, Birch and Norris,[165] on treating 5000 gallons of soda-washed Persian kerosene with 0.75 per cent by volume of fuming sulphuric acid (20% SO_3) for 45 minutes, obtained a considerable amount of acid tar. After settling, the tar was allowed to run into water and about 55 gallons of a dark reddish-brown, highly sulphurous oil separated. The separated oil was found to consist of the sulphur compounds originally present in the kerosene and those formed by reaction with the acid, together with a complex mixture of aromatic hydrocarbons from which was separated a number of pure hydrocarbons of the benzene and naphthalene series.[166]

Other organic liquids also exert a preferential solvent action on the aromatic hydrocarbons of gasolines and kerosenes. Göhre[167] suggested several solvents for the purpose. Levulinic acid, which can be used at ordinary temperatures and is readily extracted with water, gives theoretical results for the aromatic content of oils containing up to 90 per cent of these constituents. Phenylhydrazine is satisfactory for the extraction of aromatics from various oils but not from low-boiling fractions. Glycol monoacetate in the proportion of 3 parts of solvent to 1 of oil gives reliable results at ordinary temperatures for light oils and oils of medium viscosity. Furfuraldehyde in the proportion of 1 : 1 at —10° C. is a solvent for extracting all oils. Other solvents which have been proposed for removing aromatics from gasoline fractions include dimethyl sulphate,[168] diethyl sulphate,[169] a mixture of sulphoacetic acid and acetic anhydride,[170] nitroso- or cyano-substituted aliphatic hydrocarbons (for example, methyl nitrite),[171] and selenium oxychloride.[172]

In a few particular cases it is not necessary to concentrate the aromatic hydrocarbons. The oil is first fractionated to yield a narrow cut relatively rich in the aromatic hydrocarbon and this is then submitted to chemical treatment to yield the desired product. This method has been applied to toluene-containing frac-

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assigned to Edeleanu G.m.b.H. Cattaneo, *J. Inst. Pet. Tech.*, 1930, **16**, 581; Mizuta, *J. Soc. Chem. Ind. Japan*, 1932, Suppl. binding 469; *Chem. Abs.*, 1933, **27**, 1493; Kain, *Refiner Nat. Gasoline Mfr.*, 1932, **11**, 553; *Brit. Chem. Abs.* **B**, 1933, 691; Ihrig, U. S. Patent 1,871,694, Aug. 16, 1932; *Brit. Chem. Abs.* **B**, 1933, **27**, 615; Buchel and Saal, Dutch Patent 28,715, 1933; *Chem. Abs.*, 1933, **27**, 2293; Morrell and Egloff, U. S. Patent 1,868,333, July 19, 1932; assigned to Universal Oil Products Co., *Chem. Abs.*, 1932, **26**, 5201; Pyzel, *Petroleum Z.*, 1933, **29** (11); *Motorenbetrieb und Maschinen-Schmierung*, 1933, **6** (3), 5; *Chem. Abs.*, 1933, **27**, 3593; Standard Oil Development Co., French Patent 729,213, 1932; *Chem. Abs.*, 1932, **26**, 6061.

[165] *J.C.S.*, 1926, 2545.

[166] These have already been mentioned in a preceding section.

[167] *Petroleum Z.*, 1927, **23**, 73; *Brit. Chem. Abs.* **B**, 1927, 131.

[168] Valenta, *Chem. Ztg.*, 1906, **30**, 266; *Chem. Soc. Abs.*, 1906, **90** (2), 310; *Analyst*, 1906, **31**, 202; Graefe, *Petroleum Z.*, 1906, **2**, 810; *Rev. Fett- u. Harz-Ind.*, 1907, **14**, 112; *Chem. Abs.*, 1907, **1**, 1909; Harrison and Perkin, *Analyst*, 1908, **33**, 2; *Chem. Abs.*, 1908, **2**, 978.

[169] Taylor, *Ind. Eng. Chem.*, 1927, **19**, 77.

[170] Kattwinkel, *Chem. Ztg.*, 1925, **49**, 57; *Chem. Abs.*, 1925, **19**, 1113.

[171] Bataafsche Petroleum Maatschappij, German Patent 557,739, 1930; *Chem. Abs.*, 1933, **27**, 594; Dutch Patent 28,767, 1933; *Chem. Abs.*, 1933, **27**, 2293.

[172] Lenher, U. S. Patent 1,473,350, Nov. 6, 1923.

tions of gasoline rich in aromatics, for example, Borneo (Koetei) petroleum. Nitration of such fractions can be made to yield TNT.[173] The oxidation of toluene-containing petroleum distillates for the production of benzaldehyde or benzoic acid has been investigated by a number of workers (see Chapter 41). In general, however, for the production of chemical derivatives of aromatic hydrocarbons it is advantageous to start with materials as pure as possible, since the presence of aliphatic hydrocarbons frequently leads to great technical difficulties in the isolation and subsequent purification of the product.

The separation of the non-aromatic hydrocarbons of gasolines and kerosenes with various solvents has been attempted from time to time but without much success. A method of concentrating naphthenes and paraffins in gasoline fractions by differential solubility in liquid sulphur dioxide was described by Egloff, Morrell and Moore,[174] but Seyer and Gill [175] examined the solubility relationships underlying this method and found them unfavorable. Ferris [176] proposed a method for the partial concentration of paraffins and naphthenes in mineral oils with nitrobenzene, which is said to exert a greater solvent action on the naphthenic hydrocarbons. Other solvents which have been suggested for the separation of paraffin and naphthene constituents of mineral oils [177] include phenol,[178] cresylic or wood-tar acids,[179] benzaldehyde,[180] benzonitrile,[181] phenyl acetate or organic thiocyanates,[182] furfuralcohol,[183] and β,β'-dichloroethyl ether (Chlorex).[183a] Attempts have been made to separate naphthenes from paraffins by chemical treatment under such conditions that only the former are attacked. Some of the chemical treatments which have been advocated include oxidation,[184] combination of naphthenes with benzoyl chloride in the presence of aluminum chloride,[185] and the action of fuming nitric acid.[186] It is extremely likely, however, that although the normal paraffins may be unaffected by such treatments, the relatively more reactive isoparaffins will be attacked as well as the naphthenes.

THE ORIGIN OF PETROLEUM

In a work of this character it is unnecessary to consider fully the various theories which have been advanced to explain the origin of petroleum. Many of the older theories, including the inorganic (carbide) theory, have been abandoned, the evidence for an organic origin for petroleum appearing now to be almost conclusive. In addition to the geological evidence, the organic theory is supported by the chemical nature of petroleum, more especially by the presence of optically active substances, naphthenic acids, and sulphur and nitrogen compounds.[186a] Moreover, the absence of carbon monoxide, hydrogen, and olefins in natural gas and of unsaturated compounds in petroleum, as mentioned previously, appears to indicate that low-temperature processes are alone responsible. The presence of aromatic hydrocarbons in petroleum does not necessarily indicate a high-temperature synthesis since the existence of these hydrocarbons can also be explained by disproportionation [188] reactions at low temperature. The possibility that synthetic processes as a result of the action of alpha-radiation from radioactive minerals are partly responsible for petroleum formation, as suggested by Lind,[187] is rendered doubtful by the composition of petroleum and natural gas.[188]

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[173] E.g., Ruff, U. S. Patent 1,263,289, Apr. 16, 1918; assigned to By-Products Manufacturing Co.; *Chem. Abs.*, 1918, **12**, 1597.

[174] *Chem. Met. Eng.*, 1918, **18**, 396; *Chem. Abs.*, 1918, **12**, 1923.

[175] *Trans. Roy. Soc. Canada*, 1924, **18** (3), 209; *Chem. Abs.*, 1925, **19**, 917.

[176] U. S. Patent 1,788,569, Jan. 13, 1931; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1931, **25**, 1069; Ferris, Birkhimer and Henderson, *Ind. Eng. Chem.*, 1931, **23**, 753; Ferris and Houghton, *Refiner*, 1932, **11**, 560; *Chem. Abs.*, 1933, **27**, 2025; Atlantic Refining Co., British Patent 353,307, 1930; *Chem. Abs.*, 1932, **26**, 3514.

[177] This subject is discussed by Nash, *Oil and Gas J.*, 1933, **31** (45), 52; *Chem. Abs.*, 1933, **27**, 3594.

[178] Stratford and Moor, U. S. Patent 1,877,614, Sept. 13, 1932; Canadian Patent 320,423, 1932; *Chem. Abs.*, 1932, **26**, 2584; both patents assigned to Standard Oil Development Co.; Stratford, Moor and Pokorny, *Oil and Gas J.*, 1933, **31** (45), 8; *Chem. Abs.*, 1933, **27**, 3596.

[179] Tuttle, U. S. Patent 1,912,348, May 30, 1933; *Chem. Abs.*, 1933, **27**, 4070.

[180] Birkhimer, U. S. Patent 1,904,402, April 18, 1933; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 3601.

[181] Kurtz, U. S. Patent 1,899,969, Mar. 7, 1933; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 3069.

[182] Ferris, Canadian Patent 334,103, 1933; *Chem. Abs.*, 1933, **27**, 4919; U. S. Patents 1,874,946 and 1,874,947, Aug. 30, 1932; *Chem. Abs.*, 1932, **26**, 6117; all patents assigned to Atlantic Refining Co.

[183] Hill, U. S. Patent 1,883,374, Oct. 18, 1932; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 836.

[183a] Page, Buchler and Diggs, *Ind. Eng. Chem.*, 1933, **25**, 418.

[184] Charitschkoff, *Rev. Fett- u. Harz-Ind.*, 1909, **16**, 110; *Chem. Zentr.*, 1909, **1**, 1947; *Chem. Abs.*, 1909, **3**, 1699.

[185] Marcusson, *Chem. Ztg.*, 1913, **37**, 533, 550; *J.S.C.I.*, 1913, **32**, 589.

[186] Heusler, *Ber.*, 1897, **30**, 2747; *cf.* Ubbelohde, Malaxa, Agthe and Guchmann, Unpublished theses, Karlsruhe, 1910, 1912; see Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, **1**, 285; Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., 1932, 91.

Although an organic origin for petroleum is fully indicated by the evidence available, there is no general agreement as to the mechanism and the raw materials of the process. Anaerobic fermentation and destructive distillation of both animal and vegetable remains have been suggested from time to time.[189] Destructive distillation would probably yield hydrogen and carbon monoxide, which are not present in any gaseous petroleums (the unsaturated hydrocarbons, simultaneously produced during thermal dissociation processes, could be assumed to have polymerized to aromatic and saturated cyclic hydrocarbons). Oil and bituminous products resulting from the prolonged acid hydrolysis of an aqueous extract of seaweed or algae, as well as from the acid hydrolysis of sugars, calcium salts of ethereal sulphonic acids, or decomposition products of algae [190] would offer another explanation. On the whole, an anaerobic fermentation of organic material appears to be favored as the most likely mode of formation. The optical activity of some petroleums (possibly derived from cholesterol,[191] phytosterols, terpenes,[192] resins or proteins), as well as the presence of nitrogen compounds, serves in part to substantiate the fermentation theory.[193] It seems likely, however, that the several varieties of crude petroleums have been produced by somewhat different processes and from other raw materials. In some cases, the chemical character of the crude lends credence to the supposition that filtration through certain strata has resulted in a gradual separation of the more fluid and volatile hydrocarbons from the heavier and less volatile fractions. The latter would tend to be retained or adsorbed by the strata through which filtration had taken place. Undoubtedly such migration processes with attendant filtration and adsorption, would play an important rôle in determining the physical and chemical characteristics of crude petroleums.

[186a] See Clark, *J. Inst. Pet. Tech.*, 1926, **12**, 257.

[187] *Science*, 1931, **73**, 19; *Chem. Abs.*, 1931, **25**, 1469. With respect to this theory it is interesting to note that the radium content of some Russian petroleum waters has been determined; see Baronov and Kurbatov, *Compt. rend. acad. sci. U.S.S.R.*, 1931A, 171; Kurbatov, *ibid.*, 1931A, 168; Tageeva and Starik, *ibid.*, 1931A, 163; *Chem. Abs.*, 1932, **26**, 2114.

[188] Brooks, *Bull. Am. Assoc. Petroleum Geol.*, 1931, **15**, 611; *Chem. Abs.*, 1931, **25**, 4496.

[189] See Terada, Hirata, and Utigasaki, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1932, **17**, 265; *Brit. Chem. Abs.* **B**, 1932, 297; Potonié and Wichler, *Z. angew. Chem.*, 1932, **45**, 803; Berl, Biebesheimer and Dienst, *Ann.*, 1933, **504**, 38, 62; *Brit. Chem. Abs.* **A**, 1933, 929.

[190] Hackford, *J. Inst. Pet. Tech.*, 1932, **18**, 74; *Chem. Abs.*, 1932, **26**, 2674; Ginsburg-Karagicheva, *Bull. Am. Assoc. Petroleum Geol.*, 1932, **17**, 52; *Chem. Abs.*, 1933, **27**, 3595.

[191] *Zelinsky*, *Ber.*, 1927, **60**, 1793; *Brit. Chem. Abs.* **B**, 1927, 865; *cf.* Steinkopf, *J. prakt. Chem.*, 1919, (2) **100**, 65; *Chem. Soc. Abs.*, 1921, **120** (1), 24; *Ber.*, 1927, **60**, 2609; *Brit. Chem. Abs.* **B**, 1928, 148.

[192] Freund, *Petroleum Z.*, 1932, **28** (37), 1; *Chem. Abs.*, 1933, **27**, 591.

[193] Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, **1**, 211; Karrer, "Lehrbuch der organischen Chemie," Kirschwaldsche Buchhandlung, Berlin, **1930**, 41. See also, Gurwitsch-Moore, *op. cit.*, **1932**, 280; Gruse, "Petroleum and its Products," McGraw-Hill Book Co., Inc., New York, **1928**, 93.

Chapter 2

Thermal Decomposition of Hydrocarbons

The term thermal decomposition, or pyrolysis, embraces all those numerous and varied reactions which are brought about by the action of heat alone. Applied to hydrocarbons this not only involves a degradation of the molecule with the production of substances of lower molecular complexity, but must also include the frequent synthesis of more complicated molecules. Although the thermal decomposition of hydrocarbons has been studied for more than a century by many investigators, our knowledge of the processes involved and numerous products formed is still unfortunately very incomplete. Only the simpler hydrocarbons have been carefully studied and very little is known definitely of the corresponding behavior of the higher hydrocarbons.

The reasons for this lack of information about such reactions can be readily understood. The difficulty of preparing all but the simpler hydrocarbons as pure chemical individuals has proved a formidable obstacle, and the thermal decomposition of hydrocarbons generally gives rise to such a wide variety of products that their examination severely tests the ingenuity of even the most skilled investigators. Moreover, analytical methods for examining the complex gaseous and liquid mixtures produced were, until recently at any rate, simply not available. In particular, the methods of isolating and identifying olefin hydrocarbons are still most unsatisfactory. For such reasons as these, much of the work of the older investigators is marred by inaccuracies, and until recently there appeared to be an incomplete appreciation of the importance of numerous factors which exert a profound effect on the course and extent of the decomposition. It is now generally recognized that the most important factors to be considered in this regard are: temperature, duration of heating and area of heating surfaces, composition of heating surfaces, catalytic effects and pressure.

The thermal reactions of hydrocarbons were largely studied in the past from the point of view of their importance in the manufacture of coal gas, oil gas and carbureted water gas. At the present time, however, interest in these thermal processes lies in two principal directions, gasoline production and chemical synthesis. The enormous growth of commercial "cracking" operations, in which high-boiling petroleum fractions are degraded to yield quantities of low-boiling hydrocarbons, has made it possible to augment the world's supply of gasoline to meet the ever-growing demand for that product and thus to contribute vastly to the welfare of civilization. The by-products of the cracking process, more especially the cracking gas, are assuming an important position as suitable raw materials for chemical synthesis, and herein lie the vast potentialities of thermal decomposition processes. Recent researches have shown that pyrolysis is flexible and can be controlled to produce a variety of substances, especially appropriate as intermediates in the production of synthetic products. In other words, thermal decomposition is the link between relatively unreactive hydrocarbons present in petroleum and highly reactive substances useful as the bases of chemical synthesis.

In the following pages will be discussed the thermal decomposition of individual members of the four well-known series of hydrocarbons, namely paraffins, olefins, cyclic non-benzenoid hydrocarbons (naphthenes) and aromatics.[1] The reactions of each class will be summarized and the reaction mechanisms proposed will be outlined, some comparison being made with results of thermodynamic calculations. As catalysts influence greatly the course of such thermal reactions, these will also receive attention.

METHANE

As early as 1808, Dalton and Henry[2] found that when methane was repeatedly subjected to electric sparks or passed over an electrically heated platinum wire, or through a red-hot tube, it was converted, with deposition of carbon, into two volumes of pure hydrogen. The simultaneous formation of acetylene and olefins in the decomposition of methane by the action of heat or of electric sparks, was observed later by Berthelot,[3] who conducted methane through a porcelain tube heated to dull redness. He also observed the formation of small proportions of benzene and naphthalene.

Bone and Coward[4] studied the thermal decomposition of methane, ethane, ethylene and acetylene, and noticed that time of heating had a pronounced effect upon the yield and type of products. They reached the following conclusions with regard to the decomposition of methane in the presence of porcelain at temperatures between 500° and 1200° C.:

(1) Methane is the most stable of the hydrocarbons considered. It is always a principal product of the decomposition of the other three, especially above 800° C.

(2) It decomposes directly into carbon and hydrogen and the process, which is probably reversible at all temperatures, is chiefly a surface phenomenon.

(3) In the decomposition of methane, the formation of traces of acetylene and olefins can be detected only as long as the methane concentration exceeds 60 per cent. At low methane concentrations the gas continues to be resolved into its elements.

The effect of pressure on the decomposition of methane has been investigated by Warren.[5] Increase of pressure from 2 to 10 atmospheres decreased the yield of unsaturated hydrocarbons without influencing that of hydrogen, but at higher pressures the hydrogen decreased. Pressures below 1 atmosphere had little effect on either the hydrogen or unsaturated hydrocarbon yield.

The decomposition of methane in the presence of metallic magnesium was reported by Novak,[6] and Kusnetzov[7] studied the action of finely divided aluminum. The products found consisted solely of hydrogen and carbon (either free or combined as carbides).

That the decomposition of methane was a reversible reaction, $CH_4 \rightleftarrows C + 2H_2$, was demonstrated by Mayer and Altmayer.[8] They investigated this equilibrium from both directions at atmospheric pressure and at varying temperatures, with nickel, cobalt, and iron as catalysts. Their equilibrium values from 600° to 850° C. are here reproduced:

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[1] Reviews of the pyrolytic reactions of hydrocarbons have been made by Hurd ("Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., 1929); Egloff, Schaad and Lowry (*J. Phys. Chem.*, 1930, **34**, 1617; *ibid.*, 1931, **35**, 1825); Buylla (*Quím. e ind.*, 1933, **10**, 105; *Chem. Abs.*, 1933, **27**, 4525); Egloff, Bollman, and Levinson (*J. Phys. Chem.*, 1931, **35**, 3489); Frey (*Ind. Eng. Chem.*, 1934, **26**, 198).

[2] "System of Chemistry," **2**, 259; Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1852, **7**, 253; *Phil. Trans.*, 1809, **99**, 446.

[3] *Compt. rend.*, 1868, **67**, 233, 1188.

[4] *J.C.S.*, 1908, **93**, 1197.

[5] *Can. Dept. Mines, Mines Branch Rept.* **725**, 1933, 129; *Chem. Abs.*, 1933, **27**, 3597.

[6] *Z. physik. Chem.*, 1910, **73**, 513.

[7] *Ber.*, 1907, **40**, 2871.

[8] *Ber.*, 1907, **40**, 2134; *J. Gasbeleucht.*, 1909, **52**, 238.

Temp. ° C.	Per Cent CH_4	Per Cent H_2	Temp. ° C.	Per Cent CH_4	Per Cent H_2
600	31.68	68.32	750	6.08	93.92
650	19.03	80.97	800	4.41	95.59
700	11.07	88.93	850	1.59	98.41

Slater[9] observed that the physical and chemical nature, as well as the area, of the heating surface had a pronounced effect on the rate of decomposition of methane into its elements. The rate of decomposition of methane in an unpacked tube was determined. By packing the same tube with silica, magnesia, alumina, or baryta, this rate of decomposition was decreased, but it was accelerated by packing with such materials as lime, copper, carborundum, graphite, charcoal, or iron. Cantelo[10] examined the methane equilibrium both theoretically and experimentally. From a thermodynamic standpoint, under conditions of equilibrium, he found that only negligible quantities of higher hydrocarbons would be formed. Later, Cantelo,[11] from theoretical as well as experimental considerations, found that the decomposition of all higher hydrocarbons resolves itself, under equilibrium conditions above 400° C., into the methane equilibrium, $CH_4 \rightleftarrows C + 2H_2$. Of the catalysts studied by Cantelo, one consisting of asbestos, nickel, and nickel oxide was found to be extremely active, almost complete decomposition[11a] being attained at 780° C.

The methane equilibrium has also been investigated by Scheffer, Dokkum, and Al,[12] who arrived at the following equilibrium concentrations at various temperatures:

Temp. ° C.	Per Cent CH_4	Per Cent H_2	Temp. ° C.	Per Cent CH_4	Per Cent H_2
450	66.0	34.0	650	21.0	79.0
500	53.4	46.6	700	14.5	85.5
550	41.0	59.0	800	6.8	93.2
600	29.9	70.1			

Schenk and his collaborators[13] quantitatively investigated the methane-hydrogen equilibrium in the presence of iron at temperatures from 350° to 880° C. and also in the presence of cobalt in the temperature range 310° to 740° C., their experimental results being in very good agreement with those of Scheffer, Dokkum, and Al. The occurrence of a second type of equilibrium, hitherto unsuspected, in which hydrogen, methane and a carbide of nickel, iron or cobalt are in equilibrium, has been definitely established by these investigators. Above 680° C., however, this equilibrium was not encountered.

For many years the main reaction occurring during the thermal decomposition of methane was considered to be that of direct decomposition into its elements. In 1928 Fischer[14] published the results of his work on the production of liquid hydrocarbons from methane by pyrolysis. Fischer believed that by shortening the heating period and controlling the rate of cooling, methane would not be decomposed directly into its elements but could be made to yield residues such as $\cdot CH_3$, $:CH_2$ and $\vdots CH$, which would then polymerize to higher hydrocarbons. In such a process catalytic materials which hastened the attainment of the $CH_4 \rightleftarrows C + 2H_2$ equilibrium, therefore, were to be avoided. To confirm this prediction Fischer passed pure methane at high gas speeds through porcelain and quartz tubes, heated to 1000°-1200° C., and observed the formation of considerable proportions of higher hydrocarbons. Acetylene was noticed in the reaction gas while the light oil obtained consisted of unsaturated hydrocarbons, benzene, toluene, and xylene, together with naphthalene. Some tar which contained higher aromatic hydrocarbons was also formed. In this pyrolysis, the formation of carbon and hydrogen was promoted by such substances as silicic acid, tungsten, molybdenum and tin but was retarded by iron and graphite. Fischer emphasized the importance of the time of heating in such reactions. When a heating period of ⅓ second was used, higher hydrocarbons were produced, while carbon and hydrogen only were obtained on increasing the duration of heating to 60 seconds.

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[9] *J.C.S.*, 1916, **109**, 160.

[10] *J. Phys. Chem.*, 1924, **28**, 1036; 1926, **30**, 899, 1641.

[11] *J. Phys. Chem.*, 1927, **31**, 124, 246, 417.

[11a] It is interesting to note that this fact has been made the basis of a process (Farbw. vorm. Meister, Lucius and Brüning, British Patent 215,374, 1924) for making methane of 96·97% purity by passing a hydrocarbon such as hexane or ethylene, or a mixture of hydrocarbons such as oil gas, together with the theoretical quantity of hydrogen over a nickel catalyst at 350°-400° C.

[12] *Rec. trav. chim.*, 1926, **45**, 803. The stability of methane, ethane, and carbon monoxide at low temperatures has been discussed by Scheffer, *Bull. soc. chim. Belg.*, 1933, **42**, 251; *Chem. Abs.*, 1933, **27**, 5051.

[13] Schenk, Krägeloh, Eisenstrecken and Klas, *Stahl u. Eisen*, 1926, **46**, 671; *Z. anorg. allgem. Chem.*, 1927, **164**, 145. Schenk, Krägeloh, and Eisenstrecken, *Z. anorg. allgem. Chem.*, 1927, **164**, 313.

[14] *Brennstoff-Chem.*, 1928, **9**. 309.

The results obtained by Fischer were substantiated by Wheeler and Wood [15] and also by Stanley and Nash.[16] Wheeler and Wood found that a horizontal tube of quartz gave an optimum yield of benzene at 1050° C., and ethylene and butadiene were identified in the gaseous products of the reaction.[16a]

Stanley and Nash paid particular attention to the gaseous products of the reaction and found that comparatively long heating periods cause methane to decompose into its elements, this decomposition being increased by large heating surfaces and also by the use of such catalysts as iron and nickel. Porcelain, silica, and beryllia did not promote carbon formation. With short heating periods (as low as 0.4 second) at 1000°-1200° C., in the presence of silica, products similar to those described by Fischer were obtained. Thus at 1150° C. and 0.6 second heating duration, the yield of light oil and tar was 11 per cent of the methane used while acetylene and ethylene were present in the reaction gas to the extent of 8.8 per cent (based on methane); 6 per cent of methane had decomposed according to the equation $CH_4 \rightleftarrows C + 2H_2$. The yield of light oil was 4.8 per cent or 0.0281 gram per liter of methane.

A further extension of this work was carried out by Peters and Meyer,[17] who effected the conversion of methane into acetylene by subjecting it to temperatures of 1600°-3000° C. for extremely short periods. The heating elements were spirals of tungsten wire heated electrically, and alternatively, tubes of arc lamp carbon (2.5 mm. internal diameter). Heating periods as low as 0.0001 second were obtainable and in this way the conditions occurring in the electric arc were simulated in a purely thermal manner. Thus by passing a gas containing 89 per cent of methane through the tungsten spiral heated to about 2700° C. at such a rate that the heating period was 0.0003 second there was obtained a gas containing 6 per cent of acetylene. In another experiment substantially pure methane was subjected to a temperature of about 3000° C. in the tungsten spiral for a heating period of 0.0001 second and the reaction gas contained 15.4 per cent of acetylene, which corresponds to a yield of 325 grams of acetylene per cubic meter of initial gas. No benzene was found in the gases.

The mechanism of the conversion of methane into aromatic hydrocarbons has been discussed by Hague and Wheeler [18] in connection with their general theory of the thermal decomposition of normal paraffins, in which a very important

[15] *Fuel,* 1928, **7**, 535.

[16] *J.S.C.I.*, 1929, **48**, 1T.

[16a] Tanneberger (*Ber.*, 1933, **66**, 484; *Brit. Chem. Abs.* **A**, 1933, 485) obtained diacetylene by pyrolysis of methane; the presence of allylene, allene and butadiene was indicated in his product.

[17] *Brennstoff-Chem.*, 1929, **10**, 324.

[18] *J.C.S.*, 1929, 378; *Fuel,* 1929, **8**, 512, 560; *Brit. Chem. Abs.* **B**, 1930, 90.

rôle is assigned to ethylene. These workers state: "The first member of the series, methane, requires special consideration. Although the absence of a C—C linkage causes its behavior to be different from that of the higher members, its decomposition point being about 200° C. higher than that of ethane, whereas there is but a 25° C. interval between the decomposition points of the others,[18a] yet liquid hydrocarbons in quantity are produced from methane, the formation of benzene being at its optimum over the range 1000° to 1100° C. As Bone and Coward[19] have shown, the main decomposition of methane is ultimately to carbon and hydrogen. At comparatively low temperatures, however, ethylene is formed. As with other paraffins, we regard this ethylene as the source, through butadiene, of the benzene and other aromatic hydrocarbons produced. The mechanism of the early decomposition may be expressed by $CH_3{\cdot}H \rightarrow {:}CH_2 + H{\cdot}H$, two of the $:CH_2$ residues, of fugitive existence as postulated by Bone and Coward, combining to form ethylene."

De Rudder and Biedermann[20] investigated the influence of temperature on the pyrolytic production of higher hydrocarbons from methane at various pressures. Below 1000° C. only traces of ethylene and no acetylene are formed, while at 1000° C. and at atmospheric pressure 2 per cent of ethylene and 0.5 per cent of acetylene can be obtained at appropriate rates of flow. At higher temperatures reduced pressures increased the yield of ethylene and acetylene. The maximum production of ethylene (4 per cent) occurred at 1200° C. and 100 mm. pressure, under which conditions 2.5 per cent of acetylene was simultaneously produced. At temperatures above 1300° C. no ethylene was found in the products of reaction and acetylene was formed in amounts increasing with rising temperature. The amounts of acetylene formed at 1300° C. under 100 mm., at 1400° C. under 50 mm., and at 1500° C. under 50 mm. pressure were 6.62 per cent, 10.5 per cent, and 14.5 per cent, respectively. According to these investigators, quartz, Marquardt porcelain and nickel exerted no catalytic influence, while the introduction of hydrogen chloride into the reacting gas also had no effect on the reaction. Acetylene formation was always accompanied by decomposition of some of the methane into carbon and hydrogen, the amount of decomposition increasing with increase in the volume of the pyrolysis chamber.

Important additional experimental evidence regarding the nature of the reactions occurring in high-temperature pyrolysis has been put forward by Wheeler and Wood.[21] Both static experiments in silica bulbs and stream experiments through heated tubes of different materials were carried out. The rapid initial decomposition of methane in silica vessels is chiefly a surface effect but the decomposition, they found, does not proceed to an equilibrium condition by surface action on account of the formation of a protective layer of adsorbed hydrogen, which leads to the establishment of a false state of equilibrium. The shortest periods of heating, in the stream experiments, favor the formation of compounds containing two carbon atoms in their molecules, whereas by increasing the duration of heating aromatic compounds are formed at the expense of these simple molecules. Butylene and butadiene were identified in the products of the reaction at 1050° C. but neither propylene nor acetylene could be detected. The use of an iron tube in stream experiments led to the complete decomposition of the methane to hydrogen and carbon, the latter being of a bulky gritty nature. On the other hand, both silica and chrome-iron tubes favored the formation of liquid hydrocarbons to an equal extent and the carbon formed in these cases was of a lustrous foil-like variety exerting no influence on the course of the pyrolysis. An increase in the area of silica exposed per unit volume of gas had no appreciable effect on the velocity or extent of pyrolysis. Wheeler and Wood concluded that the reactions which are important in stream experiments are those occurring throughout the volume of the gas (i.e., not on the surface) when the surface effect of the reaction vessel has been inhibited by an adsorbed hydrogen layer. In iron tubes this protective layer of adsorbed hydrogen is not formed and the surface decomposition of methane to carbon and hydrogen consequently takes place at the expense of the homogeneous reaction.

[18a] These figures refer to decomposition in the presence of inert materials such as silica or porcelain.

[19] *J.C.S.*, 1908, **93**, 1197.

[20] *Bull. soc. chim.*, 1930, (4) **47**, 704; *Brit. Chem. Abs.* **A**, 1930, 1268; *Compt. rend.*, 1930, **190**, 1194; *Chem. Abs.*, 1930, **24**, 4255.

[21] *Fuel*, 1930, **9**, 567; *Chem. Abs.*, 1931, **25**, 1654. Also Wheeler, *Fuel*, 1931, **10**, 175.

The important position assigned to ethylene by Hague and Wheeler [22] in the production of aromatic hydrocarbons will be discussed more fully later but it is important to note at this stage that no mention is made in their work of the relatively greater amounts of acetylene produced at higher temperatures. The possibility of acetylene being an intermediate in the production of aromatics from benzene must not be overlooked, this conclusion having been reached by Frolich, White and Dayton,[23] who studied the cracking of substantially pure methane in the presence of quartz at temperatures above 1000° C. (highest temperature 1150° C.) and at pressures from atmospheric down to 25 mm. They found that acetylene is the main primary product of cracking but has a marked tendency to polymerize into benzene and similar compounds, as well as to decompose further into carbon and hydrogen, so that it becomes necessary to employ exceedingly short times of contact. At the lowest time of contact employed, 0.6 second, about 11 per cent of the entering methane appeared in the exit gas as acetylene. At a time of contact of 0.6 second, however, there was considerable carbon deposition and polymerization and an acetylene yield of less than 5 per cent calculated on the methane. A reduction in pressure below atmospheric, even to as low a figure as 25 mm., did not materially affect the conversion of the methane into acetylene. Since the total amount of cracking was reduced by decreasing the pressure, however, the yield of acetylene calculated on the basis of the methane cracked was somewhat increased.

At present the question as to whether ethylene or acetylene is the intermediate in the production of aromatic substances in the pyrolysis of methane is still *sub judice*. The opinion of Frolich and his collaborators that acetylene is the probable intermediate is supported by the work of Holliday and Gooderham,[24] who concluded that the decomposition of methane in silica bulbs is mainly a homogeneous reaction which, at temperatures above 900° C., proceeds in two stages, namely:

$$(1)\quad 2CH_4 \longrightarrow C_2H_2 + 3H_2$$
$$(2)\quad C_2H_2 \longrightarrow 2C + H_2$$

According to Wheeler [25] the first stage of the decomposition of methane at 1000° C. in the presence of silica surfaces consists of a homogeneous bimolecular reaction in which ethylene, and probably not acetylene, is produced.

A study of the pyrolysis of methane from the viewpoint of the production of motor fuels from natural gas, led Smith, Grandone, and Rall [26] to conclude that ethylene is the dominant product in the initial stages of the pyrolysis, other hydrocarbons being formed subsequently. The addition of hydrogen decreased the yields of higher hydrocarbons. Both acetylene and ethylene occurred in the gaseous products of the pyrolysis, the production of these gases being increased by dilution of the reactants with either hydrogen or nitrogen. Padovani and Magaldi[27] found that in the pyrolysis of methane at 1000°-1250° C. in silica tubes dilution with hydrogen causes an increase in the production of unsaturated hydrocarbons at lower rates of flow though the reverse holds at higher rates of flow. This fact may help to explain the discrepancy between the reported results of other investigators on the influence of dilution with hydrogen. According to Padovani and Magaldi, the decomposition of methane is accelerated by filling the reaction tube with fragments of porous porcelain.

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[22] *Loc. cit.*
[23] *Ind. Eng. Chem.*, 1930, **22**, 20.
[24] *J.C.S.*, 1931, 1594; *Chem. Abs.*, 1931, **25**, 5075.
[25] *Rec. trav. chim.*, 1932, **51**, 343.
[26] *Bureau Mines Rept. Investigations* 3143, 1931; *Chem. Abs.*, 1932, **26**, 279.

Kassel,[28] from his study of the thermal decomposition of methane in quartz bulbs at 700° to 850° C., however, suggested the following mechanism:

$$\begin{array}{lll}
(1) & CH_4 \rightleftharpoons & CH_2 + H_2 \\
(2) & CH_2 + CH_4 \rightleftharpoons & C_2H_6 \\
(3) & C_2H_6 \rightleftharpoons & C_2H_4 + H_2 \\
(4) & C_2H_4 \rightleftharpoons & C_2H_2 + H_2 \\
(5) & C_2H_2 \rightleftharpoons & 2C + H_2
\end{array}$$

He found that the presence of hydrogen very greatly retarded the methane decomposition. If hydrogen is present in sufficient quantities the decomposition rate varies directly with the square of the methane concentration and inversely with the cube of the hydrogen concentration.[29] This mechanism of Kassel accounts satisfactorily for the results obtained by Storch[30] on the decomposition of methane by carbon filaments. The latter observed ethane to be the earliest product of the thermal decomposition of methane. From the decomposition in a carbon-filament lamp immersed in liquid nitrogen as much as 95 per cent of the theoretical yield of ethane was obtained.

The main conclusions in regard to the thermal decomposition of methane are then as follows: Methane has great tendency to decompose into its elements but by shortening the heating time and employing temperatures above 1000° C. it is possible to prevent the further decomposition of the fugitive intermediate products of the reaction. At temperatures of 1000°-1200° C. under these conditions aromatic hydrocarbons as well as ethylene and acetylene are obtained, but at very high temperatures acetylene is the most important product. In the presence of materials such as iron and nickel it is impossible to stop the reaction at these intermediate stages and hydrogen and carbon only are formed.

ETHANE

Berthelot[31] considered that ethane on decomposition gave either ethylene and hydrogen, or acetylene, methane, and hydrogen as follows:

$$\begin{array}{lll}
C_2H_6 & \longrightarrow & C_2H_4 + H_2 \\
2C_2H_6 & \longrightarrow & 2CH_4 + C_2H_2 + H_2
\end{array}$$

The first comprehensive work was that of Bone and Coward,[32] who obtained evidence of the reactions:

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[27] *Atti III Cong. Naz. Chim. pura appl.*, 1929, 730; *Chem. Zentr.*, 1931, 1, 1742; *Brit. Chem. Abs.* A, 1931, 1030. See also Padovani, *Chimie et industrie*, Special No., March 1932, 255; *Chem. Abs.*, 1932, **26**, 3429.

[28] *J.A.C.S.*, 1932, **54**, 3949.

[29] *Cf.* Holliday and Exell, *J.C.S.*, 1929, **131**, 1066; Holliday and Gooderham, *ibid.*, 1931, **133**, 1594.

[30] *J.A.C.S.*, 1932, **54**, 4188.

[31] *Loc. cit.*

[32] *J.C.S.*, 1908, **93**, 1197.

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \longrightarrow C + CH_4 + H_2$$

On continued heating large proportions of methane were found in the gas (i.e., after 6 hours heating at 675° C. the resulting gas had the composition C_2H_2, 1.9%; C_2H_4, 0.7%; C_2H_6, 2.0%; CH_4, 54.5%; and H_2, 40.9%). To explain the high proportions of methane, Bone and Coward assumed the existence of labile residues, $\vdots CH$, $:CH_2$, and $\cdot CH_3$. "These residues," as pointed out by Bone and Coward, "which can only have a very fugitive separate existence, may subsequently either (*a*) form $H_2C:CH_2$ and $HC\vdots CH$, as the result of encounters with other similar residues, or (*b*) break down directly into carbon and hydrogen, or (*c*) be directly 'hydrogenized' to methane in an atmosphere already rich in hydrogen." It must be noted, however, that the accumulation of methane and hydrogen in the reaction is to be expected from thermodynamic considerations only, since the decomposition of all hydrocarbons should ultimately resolve itself into the equilibrium $CH_4 \rightleftarrows C + 2H_2$. At 800° C. Bone and Coward found the decomposition of ethane to be rapid, thus necessitating the use of closed tubes. After one minute heating they obtained a gas having the composition C_2H_2, 1.9%; C_2H_4, 11.2%; C_2H_6, 17.9%; CH_4, 31.3%; and H_2, 37.7%. After one hour's heating only methane (63.8 per cent) and hydrogen (36.3 per cent) were found in the system. At higher temperatures the decomposition was even more rapid. Ethane was passed through a tube at a speed such that the gas would not remain in the reaction zone longer than one-half minute. As the time of heating at 1000° C. increased, the proportion of hydrogen formed increased and the methane content decreased. Bone and Coward obtained 4 per cent of condensable hydrocarbons, calculated on the ethane, at 1000° C.

Zanetti and Leslie[33] found that the chief products of the thermal decomposition of ethane-propane mixtures were ethylene, methane, propylene, higher olefins, hydrogen, and aromatic hydrocarbons. The proportion of unsaturated hydrocarbons was found to attain a maximum at 750° C., at which temperature the formation of aromatic hydrocarbons began. Furthermore, the presence of iron in the reaction chamber was observed to inhibit the formation of aromatic hydrocarbons and favor complete decomposition. The tar obtained was examined later by Zanetti and Egloff[34] and found to contain benzene, toluene, naphthalene, acenaphthene and other aromatic hydrocarbons. Davidson[35] used a variety of catalysts in the decomposition of ethane-propane mixtures. The metals iron, nickel and cobalt accelerated the formation of carbon and hydrogen and a temperature of 850° C. was found best for the formation of liquid hydrocarbons. Davidson was the first to suggest that butadiene is probably an intermediate in the formation of aromatic compounds and suggested the scheme:

$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

The condensation of another molecule of ethylene with butadiene with elimination of more hydrogen could then yield benzene.

Williams-Gardner[36] suggested the following reactions for the decomposition of ethane at temperatures between 600° and 700° C.:

$$(1)\quad 2C_2H_6 \longrightarrow C_2H_4 + 2CH_4$$

$$(2)\quad C_2H_4 \longrightarrow 2C + 2H_2$$

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[33] *J. Ind. Eng. Chem.*, 1916, **8**, 777.
[34] *J. Ind. Eng. Chem.*, 1917, **9**, 474.
[35] *J. Ind. Eng. Chem.*, 1918, **10**, 901.
[36] *Fuel*, 1925, **4**, 430.

At 900° C. he obtained a yield of 9.5 per cent of benzene and 17 per cent of total liquid hydrocarbons. The heating surfaces were of porcelain and initial decomposition of ethane was observed at 550° C. under 450-550 mm. pressure. Acetylene was not formed in any quantity and was believed not to play an important part in the reaction.

Frey and Smith[37] noted that in the presence of silica at 575° C. ethane decomposed into ethylene and hydrogen exclusively, the reaction being of the first order over a considerable pressure range. Pease[38] studied the mechanism of the decomposition of ethane, propane and n- and iso-butanes at 625° and 650° C. at 1 atmosphere and concluded that the two main reactions were dehydrogenation and demethanation. The total rate of dissociation increased with the complexity of the molecule and the reactions were probably homogeneous gas reactions of the first order. An explanation of the relative rates of dehydrogenation and demethanation was advanced by Pease in terms of the activation energies as a function of the size of the molecule and the nature of the linkage.

Pease and Durgan[39] contributed a study of the equilibrium $C_2H_6 \rightleftarrows C_2H_4 + H_2$. It is necessary to point out that, although ethane does resolve itself into hydrogen and ethylene at temperatures above 550° C. and the reverse reaction also takes place at low temperatures, this reaction, nevertheless, is not a true equilibrium because if ethane is heated for long periods at temperatures at which dehydrogenation takes place, the system will ultimately resolve itself into the well-known methane equilibrium. That this is true of most of the thermal reactions of hydrocarbons at their cracking temperatures was demonstrated theoretically and practically by Cantelo and others. In spite of this, however, chemists visualize a form of equilibrium called quasi- or instantaneous equilibrium, of a transitory nature. In other words, at any particular instant, a system is thermodynamically stable at a particular temperature although changes may take place at the next instant. The equilibrium between ethane, ethylene, and hydrogen above 550° to 600° C. is undoubtedly an example of instantaneous equilibrium and Pease and Durgan found that their results were to some extent obscured, especially at 700° C., by the formation of methane. The values obtained for the equilibrium constants,

$$K_{\text{atm.}} = \frac{[C_2H_4][H_2]}{[C_2H_6]} \times \frac{P}{100}$$

in which P is the partial pressure in atmospheres, are given in Table 11.

TABLE 11.—*Ethane Equilibrium Constants.*

Heating Time, Min.	Temp. ° C.	Pressure, Atmos.	Composition of Gas C_2H_4	H_2	C_2H_6	CH_4	N_2	$K_{\text{atm.}}$
			Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	
30	600							
	Initial	0.9115	14.35	16.05	67.95		1.65	
	Final	0.9260	14.55	14.75	62.80	6.15	1.75	0.0316
6	650							
	Initial	0.9690	20.85	25.05	52.55		1.55	
	Final	0.9785	17.30	23.60	47.60	10.65	0.85	0.0839
5	700							
	Initial	0.9640	34.20	35.95	28.10		1.70	
	Final	0.9735	17.45	26.15	22.65	31.78	1.95	0.196

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[37] *Ind. Eng. Chem.*, 1928, 20, 948.
[38] *J.A.C.S.*, 1928, 50, 1779.
[39] *J.A.C.S.*, 1928, 50, 2715.

Hague and Wheeler[40] studied the decomposition of ethane at temperatures of 700° C. and over, in a vertical silica tube. At 700° C. the main reaction was found to be $C_2H_6 \rightarrow C_2H_4 + H_2$, 90 per cent of the ethane decomposing in this manner. At temperatures above 700° C., secondary reactions become important. It is considered likely that ethylene undergoes condensation to butadiene, which was observed at 750°, 800° and 850° C., according to the equation:

$$2CH_2{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

The formation of liquid hydrocarbons (mostly of an aromatic nature) was first noticed at 750° C., the yield increasing with rising temperature to a maximum at 900° C., when it corresponds with 21.9 per cent of the ethane used. The largest amount of distillate boiling between 80° and 90° C. was obtained at 850° C. and represented 11.2 per cent of the weight of ethane used. At 750° C. and 800° C. the liquid consisted largely of unsaturated hydrocarbons but, at 850° C. and above, the distillate was almost pure benzene, the residual oil consisting chiefly of naphthalene and anthracene.

By the pyrolysis of ethane in silica reaction tubes at 850° C. and with a period of contact of 0.05-0.10 minute, Frey and Hepp[41] obtained 10.5 per cent of volatile oils, mainly aromatic, calculated on the weight of ethane passed, while the gaseous products of pyrolysis contained 30.0 per cent by volume of unsaturated gases.

A careful study of the velocity of thermal dissociation of ethane into ethylene and hydrogen at temperatures of 600°-700° C. in copper reaction tubes was reported by Marek and McCluer.[42] Pure ethane was quickly preheated to reaction temperature and passed through a copper reactor at carefully controlled temperatures with short times of contact. The extent of pyrolysis in the reactor was determined by the difference in composition of the preheater and reaction coil samples. Under the conditions studied, namely at temperatures below 700° C. with short times of contact, ethane was found to decompose predominantly to ethylene and hydrogen; secondary reactions were negligible. The velocity constant of the decomposition of ethane, calculated from the general equation for unimolecular homogeneous gas reactions, was found to be satisfactorily represented by the following equation (temperature expressed as T° Absolute):

$$\log K_{C_2H_6} = 15.12 - \frac{15{,}970}{T}$$

The influence of temperature on the hydrogenation of ethylene to ethane[42a] could be represented by the equation,

$$\log K' = 8.79 - \frac{9140}{T}$$

which indicates that in the temperature range 600° to 700° C. the rate is approximately doubled for an increase of temperature of 25° C.

From the foregoing it can be concluded that ethane undergoes decomposition at temperatures up to 700° C. primarily into ethylene and hydrogen. At higher temperatures secondary reactions intervene with the production of methane, hydrogen, aromatic hydrocarbons, and butadiene, the ethylene yield rapidly diminishing with rise in temperature. However, in the presence of materials which promote decomposition of hydrocarbons into carbon and hydrogen, ethane undergoes almost complete decomposition even at temperatures below 700° C. into carbon and hydrogen. Complete decomposition of ethane into its elements has been found to occur in the presence of refractory material, pumice and iron at 725° C.,[43] of magnesium powder at red heat,[44] and of aluminum at its melting point,[45] and Sabatier and Senderens [46] noted the slow decomposition of ethane into its elements in contact with nickel at 325° C. A study of the thermal dehydrogenation of ethane in the presence of pumice impregnated with nickel and copper was made by Matignon, Kling, and Florentin,[47] who found that the formation of ethylene is favored by short times of contact with the catalyst and temperatures not above 600° C. In the presence of the nickel catalyst at 600° C., the composition of the cracked gas was: ethylene, 14.2 per cent; hydrogen, 22.0 per cent; ethane, 51.0 per cent; and methane, 12.8 per cent with a contact time of 42 seconds. With a longer time of contact (6.6 minutes) the composition of the cracked gas was: ethylene, 12.7 per cent; hydrogen, 40.7 per cent; ethane, 0 per cent; and methane, 49.9 per cent.

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[40] *Fuel*, 1929, **8**, 571.

[41] *Ind. Eng. Chem.*, 1932, **24**, 282.

[42] *Ind. Eng. Chem.*, 1931, **23**, 878.

[42a] The hydrogenation of ethylene in the presence of activated charcoal containing a small proportion of iron and a trace of copper at temperatures from −84° to 75° C. was studied by Schuster (*Z. physik. Chem.*, 1931, **14B**, 249; *Brit. Chem. Abs.* **A**, 1931, 1374).

Travers and Hockin [48] observed that when ethane or ethane-ethylene-hydrogen mixtures were heated to 600° C., three reactions took place:

(1) The reversible reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$;
(2) The formation of benzene and methane from ethane; and
(3) The formation of benzene and methane from ethane and ethylene.

Reactions (2) and (3) are related and are dependent upon the hydrogen concentration. Reaction (2) is endothermic, but (3) is exothermic.

An explanation of the thermal decomposition of paraffin hydrocarbons from the standpoint of free radicals has been given by Rice and his co-workers.[49] The relative strengths of the C—C and C—H bonds appear to indicate that decomposition of hydrocarbons takes place principally through the rupture of the C—C bonds; any breaking of a C—H bond must be wholly negligible compared with that of a C—C bond. The free radicals thus produced [50] can react in one of two ways: (1) decompose to form another free radical and hydrogen; or (2) take a hydrogen atom from the surrounding hydrocarbon molecule, since the probability that two free radicals will collide with each other is relatively small. The decomposition of the hydrocarbons can then take place according to chain reactions [51] in which the free hydrogen atoms or free radicals combine with the hydrogen atoms of the surrounding hydrocarbon molecules.

[43] Bradley and Parr, *Chem. Met. Eng.*, 1922, **27**, 737.

[44] Lidov and Kusnetzov, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 940; *Chem. Zentr.*, 1906, **1**, 329.

[45] Kusnetzov, *Ber.*, 1907, **40**, 2871.

[46] *Compt. rend.*, 1897, **124**, 1358; *Ann. chim. phys.*, 1905, (8) **4**, 435.

[47] *Compt. rend.*, 1932, **194**, 1040; *Brit. Chem. Abs.* **A**, 1932, 495.

[48] *Proc. Roy. Soc.*, 1932, **A**, **136**, 1; *Brit. Chem. Abs.* **A**, 1932, 701; *Chem. Abs.*, 1932, **26**, 4028; *cf.* Travers, Hockin and Pearce, *Nature*, 1931, **128**, 66; *Chem. Abs.*, 1931, **25**, 5075.

[49] Rice, *J.A.C.S.*, 1931, **53**, 1959; *Chem. Abs.*, 1931, **25**, 2967. Rice, Johnston and Evering, *J.A.C.S.*, 1932, **54**, 3529; *Chem. Abs.*, 1932, **26**, 5289. See also Rice and Herzfeld, *J.A.C.S.*, 1934, **56**, 284.

[50] Rice and Dooley (*J.A.C.S.*, 1933, **55**, 4245) showed the presence of free radicals when ethane is heated in the range 850°-950° C. The preparation of free methyl and ethyl radicals (from lead alkyls) has been studied by Paneth and Hofeditz (*Ber.*, 1929, **62**, 1335; *Chem. Abs.*, 1929, **23**, 5159); Paneth and Lautsch (*Ber.*, 1931, **64**, 2702, 2708; *Chem. Abs.*, 1932, **26**. 1232); and Simons and Dull (*J.A.C.S.*, 1933, **55**, 2696). Reactions of free ethyl radicals from the thermal decomposition of tetraethyl lead have been studied by Meinert (*J.A.C.S.*, 1933, **55**, 979).

[51] For a discussion of chain reactions see Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan and Co., London, 1926, 37. Griffith and McKeown, "Photo-Processes in Gaseous and Liquid Systems," Longmans, Green and Co., New York, 1929, 544, 586, 640; Clusius, "Kettenreaktionen," Gebrüder Borntraeger, Berlin, 1932; *Fortschr. Chem. Physik physik. Chem. Ser.* **B**, 1932, **21**, 1-73; *Chem. Abs.*, 1933, **27**, 461.

For example, in the decomposition of ethane, the primary reaction (P_1) may be represented to be the formation of two free methyl radicals:

$$(P_1)\ CH_3CH_3 \longrightarrow 2CH_3{-}$$

These can then react, in secondary reactions (S_1 and S_2), to form ethyl radicals, methane, and ethylene:

$$(S_1)\ CH_3CH_3 + CH_3{-} \longrightarrow CH_4 + CH_3CH_2{-}$$
$$(S_2)\ CH_3CH_2{-} \longrightarrow CH_2{=}CH_2 + H$$

Thus, the chain reaction (A_1) is:

$$(A_1)\ CH_3CH_3 + H \longrightarrow H_2 + CH_3CH_2{-} \longrightarrow H_2 + CH_2{=}CH_2 + H$$

This decomposition of ethane is particularly simple because only one kind of chain cycle and one carrier, namely the hydrogen atom, is involved.

With higher hydrocarbons, however, the reaction becomes more complicated because of the possibility of hydrogen atoms other than those at the end of the hydrocarbon molecule taking part. With propane, for instance, the primary reaction (P_1) would be:

$$(P_1)\ CH_3CH_2CH_3 \longrightarrow CH_3CH_2{-} + CH_3{-}$$

The secondary reactions then depend upon whether the carrier groups (H or CH_3—) react with the primary (as in S_2) or secondary (as in S_3) hydrogen atom of propane:

$$(S_1)\ CH_3CH_2{-} \longrightarrow CH_2{=}CH_2 + H$$
$$(S_2)\ CH_3CH_2{-} + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH_2CH_2{-}$$
$$\longrightarrow C_2H_6 + CH_2{=}CH_2 + CH_3{-}$$
$$(S_3)\ CH_3CH_2{-} + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH(CH_3){-}$$
$$\longrightarrow C_2H_6 + CH_3CH{=}CH_2 + H$$

The chain reactions (A_1 and A_2) are, therefore:

$$(A_1)\ CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2{-}$$
$$\longrightarrow RH + CH_2{=}CH_2 + CH_3{-}$$
$$(A_2)\ CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_3){-}$$
$$\longrightarrow RH + CH_3CH{=}CH_2 + H$$

in which the carriers (R) are CH_3— or H.

Rice, therefore, concludes that the composition of the products of the decomposition is determined almost exclusively by the chain cycle and is practically independent of the primary decomposition of the hydrocarbon. Later, Rice[52] modified these considerations, assuming that methyl and ethyl groups are the only stable radicals and that a larger radical apparently decomposes to yield one or more molecules of an olefin, and either a methyl group, an ethyl group or atomic hydrogen. The relative probability of reactions of primary, secondary and tertiary hydrogen atoms are assumed to be 1 : 2 : 10, respectively.

Schmidt and Grosskinsky[53] state that, in the pyrolysis of many normal and cyclo-paraffins, hydrogen splits out at more than one point and the resulting double linkage determines the position at which breaking of the chain subsequently occurs. The adjacent single linkage is thus strengthened while the one beyond is weakened. This alteration, they believe, continues with diminishing intensity throughout the chain. Norris[54] states that it is possible to break the C—C linkages in paraffin hydrocarbons successively by regulating the temperature and thus determine from the products of the pyrolysis the order in which the bonds yield to this influence.

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[52] *J.A.C.S.*, 1933, **55**, 3035.

[53] *Z. physik. Chem.*, 1932, **159**, 337; *Brit. Chem. Abs.* **A**, 1932, 716; *Chem. Abs.*, 1932, **26**, 3719.

PROPANE

The thermal decompositions of propane and butane have not been studied as extensively as that of methane. From a study of the pyrolysis of the propane-butane fraction of natural gas, Zanetti[55] found that the percentage of total unsaturated hydrocarbons in the resulting gas increased to a maximum at 750° C. and then decreased, this latter process being coincident with the formation of aromatic hydrocarbons and also of free hydrogen.

Pease[56] concluded that the initial decomposition of propane was unimolecular, the two main reactions being dehydrogenation and demethanation. Frey and Smith[57] found that at 575° C. in the presence of silica, no carbon was formed and the reaction was unaffected by an increase in the surface area of the silica. Under these conditions, the decomposition of propane could be represented by the three equations:

$$(1)\ C_3H_8 \longrightarrow C_2H_4 + CH_4$$
$$(2)\ C_3H_8 \longrightarrow C_3H_6 + H_2$$
$$(3)\ 2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$$

Of these, reactions (1) and (2) had fairly rapid velocities of the same order of magnitude, while (3) was much slower. Decomposition of propane in the presence of a nickel catalyst at 200°, 350°, and 405° C. led to the following changes:

$$(1)\ C_3H_8 \longrightarrow 2CH_4 + C$$
$$(2)\ C_3H_8 \longrightarrow C_3H_6 + H_2 \longrightarrow CH_4 + 2H_2 + 2C$$

of which (1) takes place at all temperatures and (2) becomes important only at higher temperatures.

Hague and Wheeler,[58] as a result of their very comprehensive work, came to the conclusion that the propane molecule undergoes decomposition in two ways, namely:

$$(1)\ CH_3CH_2CH_3 \longrightarrow CH_4 + CH_2{=}CH_2$$
$$(2)\ CH_3CH_2CH_3 \longrightarrow H_2 + CH_3CH{=}CH_2$$

At 700° C. in the presence of silica, reaction (1) proceeds to the extent of about 61 per cent, while reaction (2) proceeds to the extent of between 35 per cent and 39 per cent. At temperatures above 700° C. secondary changes largely occur, resulting in the decomposition of olefins to ethylene with the formation of butadiene and aromatics from the latter. The production of condensable liquid, which begins at about 700° C. and is still important at 1000° C., reaches a maximum at 850° C. (corresponding to 23.09 per cent of the weight of the propane used). At this temperature the part of the product distilling below 170° C. also attains a maximum value of 11.20 per cent by weight. At temperatures below 800° C. the liquid products are largely unsaturated and butadiene is found in the products at 750° C. and above. The use of porcelain tubes gave results similar to those obtained with silica tubes.

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[54] *J. Chem. Education*, 1932, 9, 1890.
[55] *Ind. Eng. Chem.*, 1916, 8, 674.
[56] *J.A.C.S.*, 1928, 50, 1779.
[57] *Ind. Eng. Chem.*, 1928, 20, 948.
[58] *Fuel*, 1929, 8, 572.

A study of the pyrolysis of propane in quartz tubes with and without catalysts and with special attention to the formation of gaseous olefins, has been made by Boecheler.[59] Experiments in quartz tubes without catalysts at temperatures of 500°-1000° C. showed that the main products of reaction were propylene, ethylene, and hydrogen and that there was an optimum temperature for the production of each gaseous olefin. The maximum propylene yield (13.7 per cent of the exit gas) was obtained at 805° C. The yield was increased by dilution with nitrogen, but dilution of the propane with half its volume of water vapor exerted no influence on the decomposition. The primary reaction was evidently dehydrogenation since an increase in the rate of flow of propane was accompanied by a decrease in the production of hydrogen and ethylene. The use of catalysts such as copper gauze, nickel gauze, and a mixture of zinc and copper, did not influence the character of the products but lowered the temperature necessary for their formation. A catalyst of 78.5 molar per cent zinc and 21.5 molar per cent chromium markedly increased propylene formation so that more of this hydrocarbon was produced at 655° C. than without a catalyst at 730° C. at a rate of flow only one-fourth of that at the latter temperature. An 11 per cent yield of propylene, based on propane, was obtained at temperatures as low as 520° C. when the propane was diluted with 67 per cent of nitrogen.

According to Ebrey and Engelder,[60] pyrolysis of propane in silica tubes at 600°-830° C. yields varying amounts of hydrogen, methane, ethane, ethylene and propylene, the unsaturated hydrocarbons being at a maximum at 770° C. Catalysts containing nickel, cobalt, chromium, or iron were found to favor the production of carbon and hydrogen.

Measurements of the rate of pyrolysis of propane in the presence of such reaction surfaces as silica or copper have shown that the reaction is homogeneous and gives velocity constants in agreement with a first order reaction. Pease and Durgan[61] found that the first order constants fall rather rapidly as reaction proceeds, probably on account of secondary changes, and that dilution with nitrogen somewhat increases the velocity of pyrolysis. The temperature coefficient of reaction was found by these workers to be about 2.75 per 25° C. and the heat of activation 65,000 cal. per mole. A careful study of the rates of pyrolysis of propane in a copper reaction coil at temperatures of 587°-679° C. was carried out by Marek and McCluer,[62] who found that the constants were in agreement with those required for a homogeneous unimolecular process. The principal reactions occurring were found to be dehydrogenation and demethanation, the rates of the two reactions being approximately the same. From the experimental results, Marek and McCluer calculated the following relationship between the temperature (T° Abs.) and the unimolecular reaction coefficient, k,

$$\log k = 13.44 - \frac{13{,}500}{T}$$

Schneider and Frolich[63] carried out work of fundamental importance on the pyrolysis of propane and other gases, the object of their experiments being the elucidation of the mechanism of the primary reactions occurring prior to aromatization. The method adopted in studying the reaction mechanism was to vary the degree of cracking within the range where accurate analysis of the products was possible and then to plot the results in such a manner that extrapolation to zero per cent cracking distinguishes the primary cracking products from the secondary ones. Obviously, those compounds whose production curves intersect the zero ordinate at a positive value are primary products and the others are secondary. The results obtained by subjecting propane to pyrolysis in silica reaction tubes at various temperatures and under atmospheric pressure are shown in the accompany-

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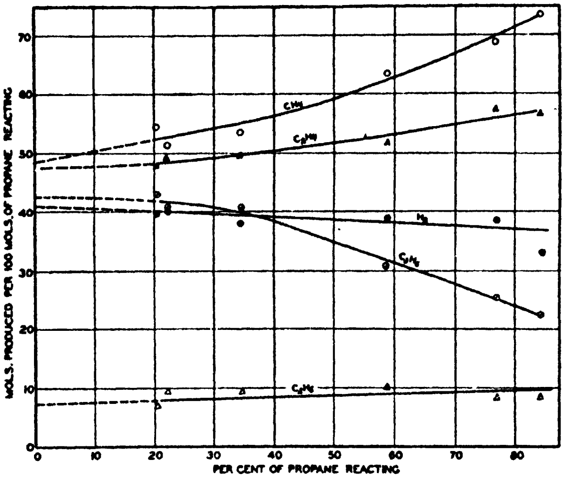
[59] Thesis, Mass. Inst. Tech., 1929, referred to by Egloff, Schaad, and Lowry, *J. Phys. Chem.*, 1930, **34**, 1685-6.

[60] *Ind. Eng. Chem.*, 1931, **23**, 1033; *Chem. Abs.*, 1931, **25**, 5977.

[61] *J.A.C.S.*, 1930, **52**, 1262.

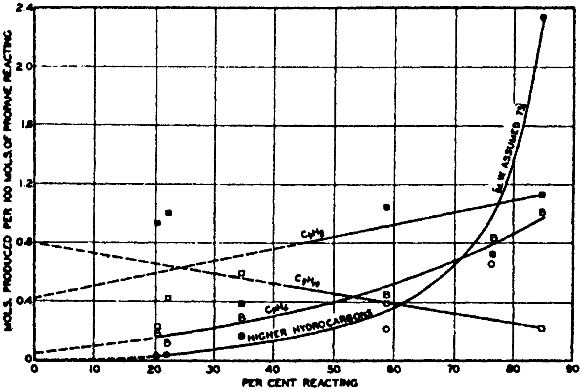
[62] *Ind. Eng. Chem.*, 1931, **23**, 878.

[63] *Ind. Eng. Chem.*, 1931, **23**, 1405.



Courtesy Industrial and Engineering Chemistry.

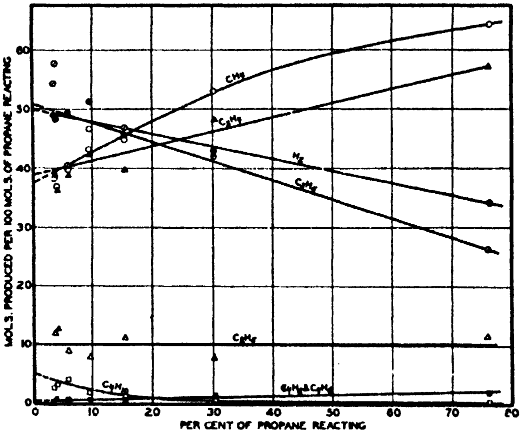
FIG. 2.—Pyrolysis of Propane at 725° C. and 1 Atmosphere. (Schneider and Frolich.)



Courtesy Industrial and Engineering Chemistry.

FIG. 3.—Pyrolysis of Propane at 725° C. and 1 Atmosphere. (Schneider and Frolich.)

ing graphs (Figs. 2, 3, and 4). It will be seen that at 725° C. and 1 atmosphere pressure, at zero per cent cracking propane decomposes to the extent of 48 per cent (molar) according to the equation $C_3H_8 \rightarrow C_2H_4 + CH_4$, while 42 per cent is converted into propylene and hydrogen according to the equation $C_3H_8 \rightarrow C_3H_6 + H_2$. Ethane also appears to be a primary product though the reaction responsible for its initial formation is not quite clear. The curves for butadiene and the higher hydrocarbons (Fig. 3) both pass through the origin, showing that these are definitely secondary reaction products. The results of cracking experiments at 650° C. and 1 atmosphere pressure (Fig. 4) show that about 50 per cent of the propane undergoes dehydrogenation to propylene and somewhat less than 40 per cent is demethanated to yield ethylene and methane. Both ethane and butane appear to be primary reaction products which may be formed according to the equation $2C_3H_8 \rightarrow C_2H_6 + C_4H_{10}$.



Courtesy Industrial and Engineering Chemistry.

FIG. 4.—Pyrolysis of Propane at 650° C. and 1 Atmosphere. (Schneider and Frolich.)

Of the two main primary reactions occurring in the pyrolysis of propane, the dehydrogenation predominates somewhat at the lower temperature studied (650° C.) but at a higher temperature (725° C.) there is a greater tendency for the C—C bond to be disrupted with the formation of ethylene and methane. The homogeneous and apparently unimolecular character of the cracking reactions was confirmed by the work of Schneider and Frolich.

Rice[64] has represented the decomposition of propane as follows: The principal reaction (P_1) produces both free ethyl and methyl radicals:

$$(P_1)\ CH_3CH_2CH_3 \longrightarrow CH_3CH_2— + CH_3—$$

The secondary reactions (S_1, S_2 and S_3) are as follows:

$$(S_1)\ CH_3CH_2— \longrightarrow CH_2{=}CH_2 + H$$

$$(S_2)\ CH_3CH_2— + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH_2CH_2— \longrightarrow C_2H_6 + CH_2{=}CH_2 + CH_3—$$

$$(S_3)\ CH_3CH_2— + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH(CH_3)— \longrightarrow C_2H_6 + CH_3CH{=}CH_2 + H$$

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[64] *J.A.C.S.*, 1931, 53, 1965.

The two chain reactions (A_1 and A_2), the relative extents of which depend upon whether the carrier group (R is CH_3— or H in this reaction) reacts with the primary (as in S_2) or the secondary (as in S_3) hydrogen atom of propane, are as follows:

$$(A_1)\ CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2{-} \longrightarrow RH + CH_2{=}CH_2 + CH_3{-}$$

$$(A_2)\ CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_3){-} \longrightarrow RH + CH_3CH{=}CH_2 + H$$

Rice has found good agreement between the experimental results of Pease and Durgan[65] and the values predicted by his theory.

In the presence of a copper-pumice catalyst[66] at 500° C., dehydrogenation to propylene is the predominant reaction and only small amounts of ethylene and methane are produced. The formation of propylene is favored by short time of contact with this catalyst, prolonged contact increasing yields of methane and ethylene.

BUTANES

Pease,[67] conducting a preliminary study of the decomposition of n-butane, concluded that demethanation and dehydrogenation were the two main reactions involved. Hague and Wheeler[68] investigated the thermal decomposition of n-butane in the presence of silica and concluded that the primary changes which take place at low temperatures (650° to 700° C.) can be represented satisfactorily by the equations:

$$(1)\ CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$$

$$(2)\ CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH{=}CH_2$$

$$(3)\ CH_3CH_2CH_2CH_3 \longrightarrow H_2 + CH_3CH_2CH{=}CH_2$$

From a careful examination of the products of the reaction it was concluded that at 650° C. in the presence of silica or porcelain about 43 per cent of butane decomposed according to reaction (1), while reactions (2) and (3) accounted for 36 per cent and 21 per cent, respectively. Liquid products of n-butane appear definitely at 700° C. and are still in evidence at 950° C. Between these two temperatures the yields attain maxima, the total oil yield at 850° C. and the "distillate up to 170° C." yield at 800° C., with values of 24.61 per cent and 12.9 per cent by weight of the butane used, respectively. At temperatures above 750° C. the distillate from the liquids obtained was almost all benzene.

Hurd and Spence[69] conducted a study of the pyrolysis of both n-butane and isobutane by passing these gases through pyrex glass tubes at 600° and 700° C. With n-butane the two main concurrent reactions at 600° C. are:

$$(1)\ CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH{=}CH_2$$

$$(2)\ CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$$

The first of these reactions is slightly favored. Two major reactions also occur in the pyrolysis of isobutane at 600° C., the formation of propylene and methane, according to the equations:

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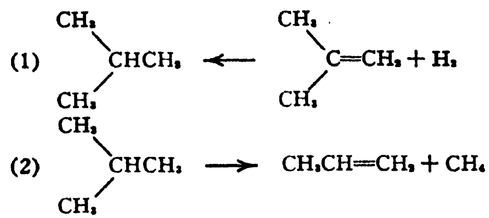
[65] *Loc. cit.*

[66] Matignon, Kling and Florentin, *Compt. rend.*, 1932, **194**, 1040.

[67] *Fuel*, 1929, **8**, 576.

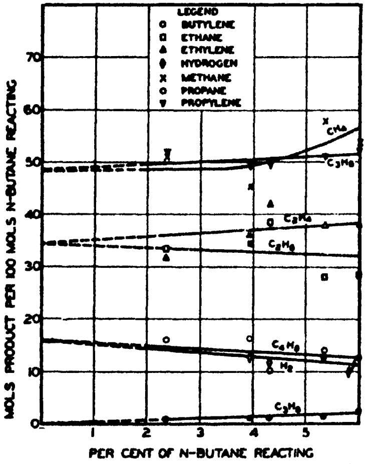
[68] *Loc. cit.*

[69] *J.A.C.S.*, 1929, **51**, 3353.



These reactions are still the major ones of n-butane and isobutane at 700° C., but secondary reactions already begin to occur at that temperature.

Neuhaus and Marek[70] have made a special study of the primary reaction products of the pyrolysis of n-butane at 600° C. and 650° C. in the presence of silica reaction surfaces. Their method was the same as that employed by Schneider and Frolich, i.e., the experimental data were plotted graphically as moles of each product formed per 100 moles of n-butane reacting against the percentage of n-butane reacting. On extrapolation to zero per cent cracked, a clear distinction between primary and secondary reaction products was obtained, the curves for secondary products passing definitely through the origin. The experimental results are shown graphically in Figures 5 and 6, from which the distribution of primary products per 100 moles of n-butane reacting was calculated as shown in Table 12.



Courtesy Industrial and Engineering Chemistry.

Fig. 5.—Cracking of n-Butane at 600° C. (Neuhaus and Marek.)

Table 12.—*n-Butane.*

	At 600° C.	At 650° C.
Methane	48.5	48.0
Propylene	48.5	48.0
Ethane	34.5	36.7
Ethylene	34.5	38.7
Hydrogen	16.0	12.3
Butylenes	16.0	12.3
Propane	0	1.0(?)

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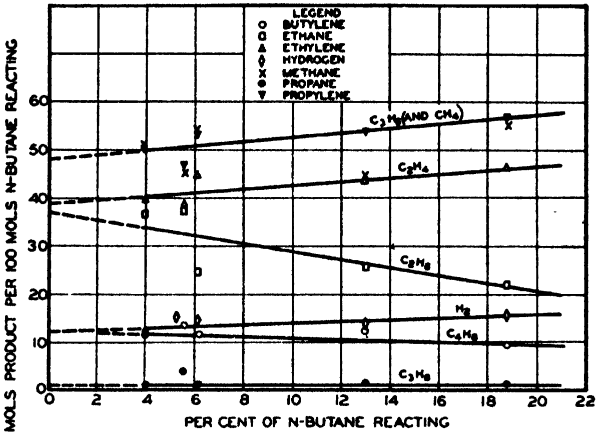
[70] *Ind. Eng. Chem.*, 1932, 24, 400.



Courtesy Industrial and Engineering Chemistry.

FIG. 6.—Cracking of n-Butane at 650° C.
(Neuhaus and Marek.)

The primary reactions, in the order of their importance, are therefore:

(1) $CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH{=}CH_2$ (about 48 per cent);
(2) $CH_3CH_2CH_2CH_3 \longrightarrow C_2H_6 + CH_2{=}CH_2$ (about 35 to 38 per cent);
(3) $CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH{=}CHCH_3 + H_2$ (about 12 to 16 per cent).[70a]

No butadiene or aromatic hydrocarbons were formed under the conditions studied and the reaction was shown to obey the equation for a first-order homogeneous gas reaction.

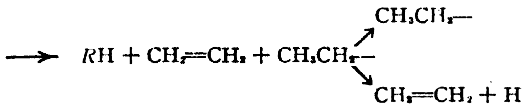
Rice [71] has represented the reactions occurring in the decomposition of n-butane as follows:

The principal reactions (P_1 and P_2) yield either free methyl, ethyl or propyl radicals:

(P_1) $CH_3CH_2CH_2CH_3 \longrightarrow CH_3{-} + CH_3CH_2CH_2{-}$
(P_2) $CH_3CH_2CH_2CH_3 \longrightarrow 2CH_3CH_2{-}$

The chain reactions (A_1 and A_2), in which the carriers (R) are $CH_3{-}$, $CH_3CH_2{-}$ or H, can then be derived and are:

(A_1) $CH_3CH_2CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2CH_2{-}$



$$\longrightarrow RH + CH_2{=}CH_2 + CH_3CH_2{-} \begin{cases} \nearrow CH_3CH_2{-} \\ \searrow CH_2{=}CH_2 + H \end{cases}$$

(A_2) $CH_3CH_2CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_2CH_3){-}$
$\longrightarrow RH + CH_3CH{=}CH_2 + CH_3{-}$

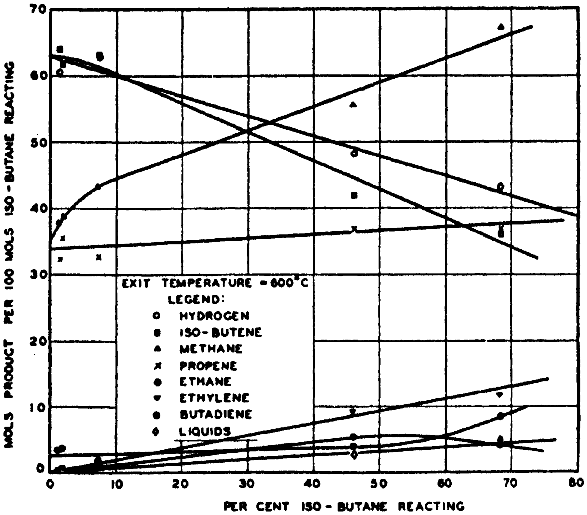
Theoretical results predicted from these reactions are in good agreement with those obtained by Pease and Durgan.[72]

[70a] The butylenes formed appeared to consist of about 20 per cent 1-butene, the remainder being 2-butene.
[71] *J.A.C.S.*, 1931, 53, 1967.
[72] *J.A.C.S.*, 1930, 52, 1266.

If the ratio of reaction (2) to reaction (1) of Neuhaus and Marek (see above) is compared with the values predicted by Rice, the following agreement is calculated:

$$\text{Ratio}\left\{\frac{\text{Reaction (2)}\quad C_2H_6 + CH_2{=}CH_2}{\text{Reaction (1)}\quad CH_4 + CH_3CH{=}CH_2}\right.$$

Temp. ° C.	Predicted by Rice	Found by Neuhaus and Marek
600° C.	0.75	0.71
650° C.	0.79	0.79



Courtesy Industrial and Engineering Chemistry.

Fig. 7.—Products Formed in the Thermal Decomposition of Isobutane at 600° C. (Marek and Neuhaus.)

The thermal decomposition of isobutane at 600° and 650° C. in silica tubes was later studied by Marek and Neuhaus.[73] The results are represented graphically in Figures 7 and 8, and the distribution of primary reaction products per 100 moles of isobutane reacting is shown in Table 13.

Table 13.—*Isobutane.*

	At 600° C.	At 650° C.
Hydrogen	63.0	63.0
Isobutylene	63.0	63.0
Methane	35.0	36.0
Propylene	34.0	36.0
Ethane	2.5	1.5

The primary reactions in order of their importance are:

(1) $(CH_3)_3CH \longrightarrow (CH_3)_2C{=}CH_2 + H_2$ (63 per cent)

(2) $(CH_3)_3CH \longrightarrow CH_3CH{=}CH_2 + CH_4$ (about 34 to 35 per cent).

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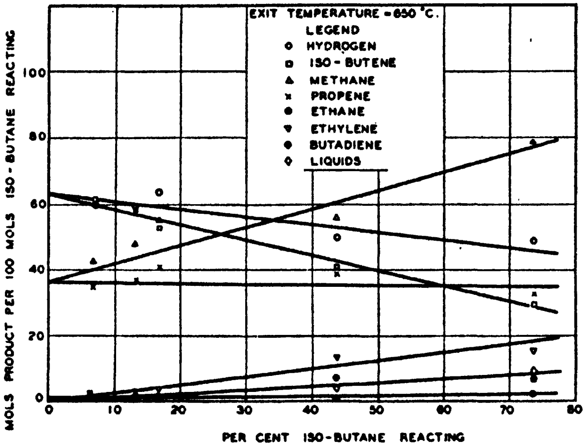
[73] *Ind. Eng. Chem.*, 1933, 25, 516.

The agreement of these experimental results with the predictions of Rice[74] are not as good as in the pyrolysis of n-butane. The ratios of the number of moles of isobutane reacting to form methane and propylene to the number of moles reacting to form hydrogen and isobutylene are as follows:

$$\text{Ratio}\left\{\frac{\text{Reaction (2)}\quad CH_4 + C_3H_6}{\text{Reaction (1)}\quad H_2 + C_4H_8}\right.$$

Temp. ° C.	Predicted by Rice	Determined
600° C.	0.91	0.55
650° C.	1.04	0.57



Courtesy Industrial and Engineering Chemistry.

FIG. 8.—Products Formed in the Thermal Decomposition of Isobutane at 650° C. (Marek and Neuhaus.)

A detailed examination of the volatile oils obtained from the pyrolysis of a mixture of 89 per cent n-butane and 11 per cent isobutane at 850° C. in silica reaction tubes has been made by Frey and Hepp,[75] who found the oil to contain propylene, butenes (chiefly isobutene), 1,3-butadiene, pentenes, cyclopentadiene, hexadienes, methylcyclopentadiene, benzene, toluene, xylenes and styrene.

From a study of the kinetics of the pyrolysis of the butanes, Pease and Durgan[76] concluded that the processes involved are fundamentally first order homogeneous gas reactions, though the velocity coefficients fall rapidly as pyrolysis proceeds. At low pressures the constants are distinctly less than at 1 atmosphere. Dilution with nitrogen increases the velocity constants to some extent.

In the course of a study of the thermal dehydrogenation of gaseous paraffin hydrocarbons in the presence of copper and nickel on pumice, Matignon, Kling, and Florentin[77] found that at 500° C. with a copper catalyst, the predominant reaction is

$$C_4H_{10} \longrightarrow C_3H_6 + CH_4 - 17\text{ Cals.},$$

[74] *J.A.C.S.*, 1931, 53, 1959.

[75] *Ind. Eng. Chem.*, 1932, 24, 282.

[76] *J.A.C.S.*, 1930, 52, 1262.

[77] *Compt. rend.*, 1932, 194, 1040.

while about 20 per cent decomposition occurs according to the equation

$$C_4H_{10} \longrightarrow C_4H_8 + H_2 - 32.7 \text{ Cals.}$$

On the other hand, the reaction

$$C_4H_{10} \longrightarrow C_2H_6 + C_2H_4 - 16.4 \text{ Cals.}$$

does not occur below 520° C. (using a copper catalyst) but is markedly favored by rise in temperature, becoming predominant at 600° C.

PENTANES

Norton and Andrews[78] were among the first to investigate the thermal decomposition of pentane and concluded that, at a "red heat," ethylene, propylene, butadiene and paraffin hydrocarbons were produced but no benzene. A more precise investigation of the pyrolysis of n-pentane and isopentane at 600° C. was made by Calingaert.[79] The unsaturated hydrocarbons in the exit gas were examined by bromination methods, followed by fractionation of the resulting olefin bromides. It was considered that the n-pentane molecule was disrupted at the central carbon atom, giving ethyl and propyl groups, one of which was saturated at the expense of the other. Of the n-pentane decomposed, Calingaert concluded that about 55 per cent follows the reaction:

$$(1)\ CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_3CH{=}CH_2$$

25 per cent decomposes according to the reaction:

$$(2)\ CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_3 + CH_2{=}CH_2$$

and most of the remainder decomposes to methane and butylene:

$$(3)\ CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH_2CH{=}CH_2$$

Calingaert found that at 600° C. the isopentane molecule was disrupted on one or the other side of the tertiary carbon atom giving: in the first case, a methyl and isobutyl group (which, by saturation of the lighter group, yields methane and 1- or 2-butene) and, in the second case, an ethyl and an isopropyl group, the ethyl group always becoming saturated since no ethylene was found. Besides these two reactions a small amount of amylene was formed. Thus isopentane yields methane and the butylenes by one reaction and ethane and propylene by a second.

Hague and Wheeler[80] concluded from their work that the important changes in the pyrolysis of n-pentane up to 700° C. appear to be demethanation, dehydrogenation and "de-ethylenation" (a word coined to express the elimination of ethylene). The extent to which the olefins are eliminated, and also their character, was rather uncertain. Contrary to the experience of Calingaert, the gas mixture obtained at 600° C. contained methane, ethylene, and higher olefins in proportions decreasing in that order. At higher temperatures aromatic hydrocarbons were formed, the best yields being at 850° C., corresponding to a total yield of oil of 26.80 per cent by weight of the pentane, of which 11.87 per cent distilled over between 80° and 90° C.

Norris and Thomson[81] have made careful measurements of the effect of temperature upon the rate of pyrolysis of n- and isopentanes in the region of incipient dissociation. The hydrocarbons were heated in the vapor phase for about one hour at a definite temperature in a glass apparatus in which the expansion occurring under atmospheric pressure could be measured. At temperatures below those of decomposition, no expansion was evident after the attainment of thermal equilibrium. As the temperature was raised, step by step, a temperature was reached at which a definite expansion due to pyrolysis continued throughout the hour. The results obtained with n-pentane are shown in Figure 9, from which it will be seen that the initial temperature of pyrolysis is about 391° C. Since one definite break in the curve occurs at 423° C. and another at 451° C., Norris and Thomson believed it likely that one type of decomposition takes place in the range 389°-423° C., another between 423° and 451° C., and the greatly increased rate above 451° C. indicates more profound cracking of still a third kind. Experiments (not reported) were stated to indicate that at 10° above the initial cracking temperature, as observed by the above method, a simple decomposition takes place as the result of the fission of a C—C bond. In the case of isopentane the initial cracking temperature was found to be 383° C. and two breaks, at 423° and 450° C., were revealed on the cracking curve.

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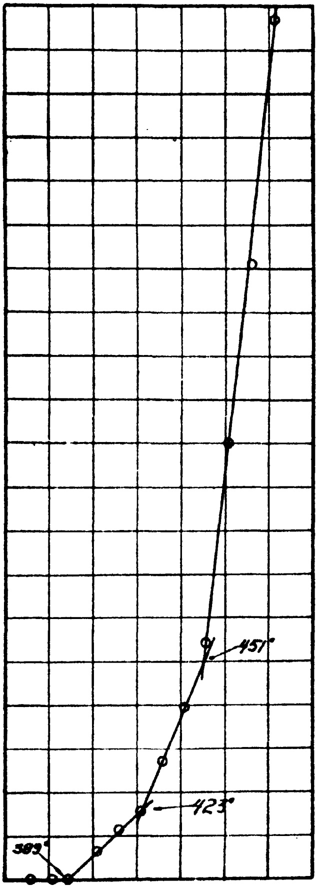
[78] *Amer. Chem. J.*, 1886, 8, 1.
[79] *J.A.C.S.*, 1923, 45, 130.
[80] *Fuel*, 1929, 8, 580; *J.C.S.*, 1929, 378.
[81] *J.A.C.S.*, 1931, 53, 3108.



Courtesy Journal of the American Chemical Society.

FIG. 9.—n-Pentane Cracking Rate Curve. 1 Scale Division = 0.09 cc. at 40° C. (Norris and Thomson.)

HEXANE

Norton and Andrews[82] found that no gas was evolved from hexane at 550° C., but at 600° C. decomposition had begun and at 700° C. a liquid, thought to contain pentene and hexene, was obtained. At 700° C. propylene and butylenes were noticed in the gas but no ethylene. Benzene was formed at a bright red heat. Haber[83] reported that at temperatures between 600° and 800° C., n-hexane decomposes with the elimination of methane according to the equation:

$$CH_3CH_2CH_2CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH_2CH_2CH{=}CH_2$$

This dissociation he regarded as typical of the paraffin hydrocarbons.

Ipatiev and Dowgelewitsch[84] obtained ethylene, propylene, possibly isobutylene, and paraffin hydrocarbons by decomposing hexane in an iron tube at 650°-700° C. At 710° C. the gas contained 50 per cent unsaturated and 41.6 per cent saturated hydrocarbons together with 8.4 per cent hydrogen, and a 75 per cent yield of liquids boiling at 37° to 72° C. was also recovered.

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[82] *Amer. Chem. J.*, 1886, 8, 1.
[83] *Ber.*, 1896, 24, 2691.
[84] *Ber.*, 1911, 44, 298.

Hague and Wheeler[85] found that the thermal decomposition of n-hexane was appreciable in the presence of silica at 600° C., but a complete mechanism of the decomposition could not be advanced owing to difficulties in the estimation of the amylenes and butylenes. At temperatures up to 700° C. the important constituents of the gaseous products were methane, ethylene, higher olefins, and hydrogen in that order. From the high proportion of methane obtained, the principal reaction appeared to be:

$$CH_3CH_2CH_2CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH_2CH_2CH{=}CH_2$$

in agreement with the results of Haber. The general results were similar to those obtained from n-pentane, the important changes probably being demethanation and de-ethylenation, although dehydrogenation was of far less importance. The production of aromatic liquids was at its maximum between 800° and 850° C. The total yield of oil at 850° C. was 33.8 per cent of the weight of hexane used and, of this, 19.0 per cent represented light fraction.

HIGHER PARAFFIN HYDROCARBONS

Very little work has been carried out apparently on the thermal decomposition of paraffin hydrocarbons possessing more than 6 carbon atoms, a fact which can be ascribed partly to the difficulty of preparing such hydrocarbons in the pure state and partly to difficulties in the analysis of the products of reaction.

Vohl[86] advanced the view that the higher paraffins were decomposed initially into a paraffin of high molecular weight and an olefin of low molecular weight but this theory is now regarded as untenable in the light of more recent work.

The first work of importance was that of Thorpe and Young,[87] who studied the effect of distilling a paraffin wax of melting point 46° C. (containing C, 85.14 per cent; H, 14.81 per cent) under a pressure of about 2 atmospheres. Besides a comparatively small amount of gas the products were liquids, boiling for the most part between 100° and 300° C., while only 7 per cent boiled between 18° and 100° C. It was found that in the lower fractions the liquid consisted of approximately equal proportions of paraffin and olefin hydrocarbons and that the higher fractions had a somewhat lower paraffin content. Thorpe and Young concluded that there was a decided tendency for the high molecular weight paraffin to undergo a symmetrical scission of its molecule with the production of equal parts of lower paraffin and olefin. Assuming, for the sake of simplicity, that this may occur as low down the series as butane, it was concluded that the primary decomposition was:

$$CH_3CH_2{-}CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$$

Among the products identified were amylene, pentane, hexene, hexane, heptene, heptane, octene, octane, nonene, nonane, undecene, undecane, and possibly caprylidene but no trace of benzene was found.

Tocher[88] studied the thermal decomposition of octane, decane and several paraffin distillates from the point of view of determining the value of these materials for oil-gas manufacture. He concluded that at low temperatures octane and decane are decomposed into ethylene and higher olefins, methane and hydrogen, while at higher temperatures no higher olefins are formed, the gaseous products being simply ethylene, methane, and hydrogen.

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[85] *Fuel*, 1929, 8, 583; *J.C.S.*, 1929, 378.
[86] *Polytechn. J.*, 1865, 177, 58.
[87] *Proc. Roy. Soc.*, 1871, 19, 370; 1872, 20, 488; *Ann.*, 1873, 165, 1.
[88] *J.S.C.I.*, 1894, 13, 231.

It is doubtful whether the primary products of decomposition were actually observed by Tocher. Haber[89] in 1896, in his work on the pyrolysis of hexane already mentioned, reached several other important conclusions which must now be considered. The decomposition of a paraffin molecule was believed to give rise primarily to a paraffin and an olefin. From hexane, pentene and methane were formed, but secondary reactions intervened, obscuring the result, and there may have been a condensation of the unsaturated residues to form higher molecular weight substances. Haber concluded that there is a lack of equilibrium in processes of this type, this being in agreement with the later conclusion of Cantelo[89a] that the thermal decomposition of all higher hydrocarbons at temperatures above about 500° C. ultimately resolves itself into the equilibrium

$$CH_4 \rightleftharpoons C + 2H_2$$

Worstall and Burwell[90] examined the decomposition of an impure heptane-octane mixture in a Pintsch-gas retort heated externally to about 900° C. With the possible exception of some ethane, methane was the only paraffin constituent of the gas, while the main products in the compression liquid and tar were unsaturated and aromatic hydrocarbons. Comment was made by these workers on the remarkable qualitative similarity of the products obtained by decomposing various types of raw hydrocarbon materials under these conditions.

Work of importance on this subject was contributed by Engler and Spanier,[91] who passed fractions of an American kerosene corresponding to paraffin hydrocarbons of 9 to 16 carbon atoms through a glass tube 80 cm. long, heated to temperatures of 460°-480° C., and found the gas obtained consisted chiefly of gaseous paraffins with only relatively small amounts of hydrogen. Some of the results of these investigators are given in Table 14.

TABLE 14.—*Pyrolysis of Fractions of American Kerosenes.*

B.P. Fraction, ° C.	Approx. Formula	Oil Used Cc.	Time of Run Mins.	Temp. ° C.	Gas Cc.	Analysis of Reaction Gas Unsat.	Sat.	H_2
150–180	C_9H_{20}	35	45	450–460	750	8.0	91.4	0.0
	to	35	45	470–480	850	17.8	82.2	0.0
	$C_{11}H_{24}$	35	45	480–490	1100	19.7	78.3	1.9
		35	45	490–500	1100	39.1	56.9	4.0
200–230	$C_{11}H_{24}$	50	71	460–470	400	14.4	85.6	0.0
	to	39	66	470–480	600	30.8	67.7	1.5
	$C_{13}H_{28}$	28	40	480–490	1100	46.6	50.3	3.0
250–280	$C_{14}H_{30}$	50	65	450–460	850	23.5	76.4	0.0
	to	43	60	460–470	850	32.6	67.3	0.0
	$C_{16}H_{34}$	34	50	470–480	1050	39.0	59.3	1.7
		39	55	480–490	1200	44.5	53.0	2.5

Experiments carried out with n-heptane and n-octane by these same investigators gave results as in Table 15.

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[89] *Ber.*, 1896, **29**, 2691.

[89a] *Loc. cit.*

[90] *Am. Chem. J.*, 1897, **19**, 815.

[91] Dissertation, Karlsruhe, 1910; Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, **1**, 574.

TABLE 15.—*Decomposition of n-Heptane and n-Octane.*

Substance	Temp. ° C.	Oil Used Cc.	Time of Run Mins.	Gas Formed Cc.	Analysis of Reaction Gas Unsat.	Sat.	H_2
Heptane	470–480	10	24	70	1.5	98.5	0.0
	480–490	10	20	70	1.4	97.7	0.9
Octane	460–470	10	30	70	1.4	98.6	0.0
	470–480	10	30	70	1.9	97.5	0.6
	480–490	10	30	100	1.7	97.5	0.8

When, in another series of experiments, heptane was heated to 480° to 490° C., 500° to 510° C., and 520° to 530° C., the amounts of hydrogen in the reaction gas were 3.6 per cent, 3.9 per cent and 10.2 per cent, respectively.

This work of Engler and Spanier shows very clearly that the initial course of the decomposition of the higher paraffins is such that the lower paraffins are first eliminated. The production of appreciable quantities of hydrogen does not take place until higher temperatures are attained and presumably as a result of secondary changes.

Egloff and Moore [92] examined the thermal decomposition of the following fractions of a Pennsylvania paraffin-base petroleum: (1) up to 150° C., (2) 150° to 200° C., (3) 200° to 250° C., and (4) above 250° C., the last fraction being separated into two cuts by distillation *in vacuo*. Each of these fractions was passed at the same rate through a tube-furnace at 700° C. Some of the results are given in Table 16.

TABLE 16.—*Decomposition of Pennsylvanian Petroleum Fractions at 700° C.*

B.P. Fraction ° C.	Original Oil Recovered	Original Oil Converted to Gas and Carbon	Liters of Gas Formed per Liter of Oil
	Per Cent	Per Cent	
Up to 150	2.3	97.7	710.2
150–200	29.3	70.7	560.7
200–250	66.7	33.3	420.4
150–200/*vacuo*	25.0	75.0	476.7
200–250/*vacuo*	20.0	80.0	514.4

Egloff and Moore considered that these results demonstrated that the hydrocarbons boiling between 200° and 250° C. and of the empirical formula $C_{12}H_{26}$ to $C_{16}H_{32}$ were more stable thermally than either the higher-boiling or lower-boiling fractions of the same petroleum. This conclusion, however, needs more confirmation since there may be another explanation of the above results. Furthermore, it is doubtful whether such conclusions could be validly applied generally to the paraffin hydrocarbons because the higher fractions of even a paraffin-base petroleum undoubtedly contain hydrocarbons of other series.

Gault and Hessel [93] examined the thermal decomposition of hexadecane at various temperatures and in furnaces of various lengths. It was found that in the gaseous products, the unsaturated hydrocarbons increased to a maximum at about 540° C. and then decreased regularly. The proportion of saturated hydrocarbons in the gas passed through a minimum at 615° C., while, as usual, the hydrogen content increased with rise in temperature. They believed that the following reactions took place:

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[92] *Chem. Met. Eng.*, 1917, 16, 47.

[93] *Compt. rend.*, 1924, 179, 171; *Ann. chim.*, 1924, 2, 319; *Chem. Abs.*, 1925, 19, 966. See also Seyer, *J. Inst. Pet. Tech.*, 1933, 19, 779.

(a) Hexadecane distilled undecomposed at 390° C.

(b) Saturated and unsaturated gaseous and liquid hydrocarbons were obtained at 470° C., though no hydrogen was formed at this temperature. Reactions at this temperature were represented by:

$$(1)\ RCH_2CH_2CH_2R' \longrightarrow RCH{=}CH_2 + CH_3R'$$
$$(2)\ CH_3(CH_2)_{14}CH_3 \longrightarrow CH_3(CH_2)_{12}CH{=}CH_2 + CH_4$$
$$(3)\ CH_3(CH_2)_{14}CH_3 \longrightarrow CH_3(CH_2)_{12}CH_3 + C_2H_4$$

(c) At 540° C. another reaction occurs in which hydrogen is formed:

$$RCH_2CH_2CH_2R' \longrightarrow RCH{=}CH_2 + CH_2{=}CHR' + H_2$$

(d) At 685° C. not only hydrogen but also aromatic hydrocarbons were produced. The latter are apparently the result of the following transformations:

Olefins $\longrightarrow$ Cyclohexane $\longrightarrow$ Cyclohexene $\longrightarrow$ Cyclohexadiene $\longrightarrow$ Benzene

Some aromatics (benzene) may possibly have been formed by the polymerization of acetylene.

Waterman and his collaborators[94] have done much work on the decomposition of Rangoon paraffin wax both under ordinary and increased pressure. Special attention was given to the decomposition which occurs at relatively low temperatures (327°-385° C.) under normal pressure. Thus, when 90 grams of Rangoon paraffin wax were heated to 385° C. for several hours there was produced a gas containing 18.5 cc. of hydrogen, 62.3 cc. of methane, 253.3 cc. of methane homologues (n in $C_nH_{2n+2} = 2.94$) and 167.1 cc. of unsaturated hydrocarbons (n in $C_nH_{2n} = 2.68$). The production of hydrogen in this initial stage of the decomposition is worthy of note.

The primary decomposition reactions of 2,3-dimethylbutane and n-hexane, as well as those of n-butane, isobutane, n-pentane, isopentane and 2,2-dimethylpropane in a silica tube at 575° C. were studied by Frey and Hepp.[95] Scission of the carbon chain resulted in the formation of a molecule of paraffin and a molecule of the complementary olefin (i.e., the olefin which results from the splitting out of the paraffin) when the paraffin formed was methane. When a higher paraffin was produced, part of it appeared as the corresponding olefin and hydrogen. n-Pentane and n-hexane, however, did not give equal proportions of complementary products, their behavior being in accordance with a chain-reaction mechanism postulating the formation and subsequent decomposifion of free alkyl radicals. When olefins were produced by splitting of the side-chain, the ethylene linkage was in the inner position and not at the end of the chain. The normal paraffin yielded only 1-olefins. 2-Butene was found in both isomeric forms (trans- and cis-2-butenes).

SUMMARY OF THERMAL REACTIONS OF PARAFFIN HYDROCARBONS

The conclusions to be drawn from the preceding outline of the decomposition of the paraffins may be briefly summarized as follows:

(1) Methane is the most stable of the paraffins and is always an important product of the thermal decomposition of all other hydrocarbons. Both from a theoretical and practical point of view there is reason to believe that at temperatures above about 500° C. (except perhaps at very high temperature when acetylene appears to be stable) the decomposition of all hydrocarbons resolves itself into the methane equilibrium $CH_4 \rightleftarrows C + 2H_2$. It should be pointed out, however, that this is an ultimate condition which is attained only after considerable

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[94] Waterman, Perquin and van Westen, *J. Inst. Pet. Tech.*, 1928, 14, 318; *ibid.*, 1930, 16, 29.

[95] *Ind. Eng. Chem.*, 1933, 25, 441.

time in the absence of active catalysts, and is never approached in commercial cracking operations.

(2) The most striking feature of the thermal decomposition of the paraffin hydrocarbons up to hexane (and probably also throughout the series), is the similarity of their behavior at the higher temperatures. Below approximately 750° C. the primary decompositions are taking place and each hydrocarbon follows its own special course, but at higher temperatures similar products are obtained, namely ethylene (whose production attains a maximum at about 700°-750° C. except in the case of methane), butadiene, and aromatic hydrocarbons as well as hydrogen, methane and carbon.

(3) The work of Hague and Wheeler on the pyrolysis of the paraffins up to hexane showed that the primary decomposition of the paraffins results in a rupture of the chain at any position with the production of an olefin and the complementary lower paraffin, or, in the limit, of hydrogen. As the series is ascended, the tendency for hydrogen to be eliminated leaving an olefin with the same number of carbon atoms rapidly diminishes. Carbon is never produced in the primary stage of the reaction.

(4) As regards the stability of the higher paraffin hydrocarbons, too little work has been carried out for a generalization to be made. From the work of Egloff and Moore it appears that paraffins having 12 to 15 carbon atoms are more stable than their immediate homologues but this requires confirmation. It is certain, however, that the higher solid paraffins are much less stable, their decomposition occurring at much lower temperatures. Little is known, moreover, of the mode of decomposition of the higher paraffins. Burrell[96] has concluded that at comparatively low temperatures symmetrical splitting of the molecule takes place with the production of approximately equal amounts of paraffin and olefin of nearly equal molecular weight, while higher temperatures cause the splitting off of lower paraffins (methane and ethane, for example) with the formation of high molecular weight olefins. The work of Engler and Spanier is consistent with the view that decomposition takes place with the splitting off of the lower paraffins, the production of hydrogen being very small. It is true that Waterman and his co-workers noted the production of hydrogen from paraffin wax at 385° C., but much larger amounts of gaseous saturated hydrocarbons were simultaneously formed. It is probable also that molecular constitution greatly influences the course of thermal decomposition of the higher paraffins.

(5) Most of the foregoing conclusions are only valid when the thermal decomposition takes place in the presence of inactive materials such as silica, porcelain, or glass. Substances such as iron and nickel tend greatly to hasten the attainment of the ultimate state of equilibrium (as distinct from simultaneous, or quasi-equilibrium) which, in the case of hydrocarbons above 500° C., can be represented by $CH_4 \rightleftarrows C + 2H_2$. Certain catalysts, moreover, have a specific action in accelerating some types of reactions and not others. The action of aluminum chloride in splitting off gaseous paraffin molecules is noteworthy in this respect. (See Chapter 6). The time of heating and the area, as well as nature, of the heating surface are also factors which must be taken into consideration.

Thermodynamic Considerations. By using the Nernst Heat Theorem it is possible to calculate from thermal data alone the equilibrium constants of all possible (and also impossible) reactions at various temperatures. Given the necessary thermal data, one can calculate (1) which of several possible reactions leads to the most stable state of a system, (2) whether a conceivably possible reaction can actually occur, (3) the magnitude of the driving force tending to cause the reaction to proceed, and (4) the conditions of equilibrium in the system for the reaction under consideration.

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[96] *Ind. Eng. Chem.*, 1928, 20, 602.

It is of importance to note, however, that the laws of thermodynamics tell us nothing whatever about the relative velocities with which reactions take place, the rate of chemical change depending on a number of factors, notably on the presence of catalytic materials. By the aid of thermodynamics, calculations of free energies of hydrocarbons and of equilibrium constants of cracking reactions have been made by a number of workers and conclusions drawn from them regarding the thermal decomposition of the paraffin hydrocarbons.

Francis,[97] from a calculation of free energies of hydrocarbons at various temperatures, arrives at the following conclusions in regard to the paraffins.

(1) At low temperatures, paraffins are more stable than olefins with the same number of carbon atoms, while at high temperatures the olefins are more stable.

(2) The direct production of higher hydrocarbons from lower ones, except with simultaneous formation of still lower ones in at least equivalent amount, is thermodynamically impossible.

(3) Dissociation of paraffins to hydrogen and olefins of the same number of carbon atoms can occur at higher temperatures but under these conditions (700° C.) more complete disruption of the molecule is favored.

(4) Of all the hydrocarbons, the paraffins are least stable at higher temperatures.

Sachanen and Tilicheyev[98] from a calculation of the equilibrium constants of various cracking reactions at 477° C. reached the conclusion that the tendency of paraffins to break at the middle of the chain (with production of lower paraffin and olefin of almost the same molecular weight) increases with increase in the molecular weight of the paraffin concerned. The other conclusions of Francis were substantiated.

When the above deductions from thermodynamic laws are compared with the results of experiment it will be found that, in the main, there is good agreement. It must be pointed out, however, that the deductions from thermodynamic equations may be nullified merely by taking advantage of the slowness of the decomposition of some compounds, as was done by Fischer and other investigators on the production of higher hydrocarbons from methane.

THERMAL DECOMPOSITION OF OLEFINS

Ethylene

Dalton and Henry[99] in 1808 observed that when electric sparks were passed for some time through ethylene, it was resolved into carbon and two volumes of hydrogen. Deiman, van Troostwyk, Bondt and Lauwerenburgh[100] reported that a red heat acted like electricity except that it converted a portion of the gas into marsh gas (methane) and an aromatic oil. They noticed that when metals were present these were converted into carbides. Sefström[101] used heated iron wire, and Marchand[102] employed porcelain fragments, as well as copper, nickel and platinum, to effect decomposition.

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[97] *Ind. Eng. Chem.*, 1928, 20, 277.

[98] *Ber.*, 1929, 62, 658. The surname of Dr. A. N. Sachanen is transliterated and written in various ways—it occurs as *Sakhanov*, *Sachanow*, and *Sackanoff* in some indices, and that of his collaborator, M. D. Tilicheyev, as *Tillichéev*, *Tilischejew*, *Tilicejev*, and *Tilicheyeff*.

[99] See Gmelin, "Handbook of Chemistry," Translated by Watts, Cavendish Society, London, 1853, 8, 165; *Phil. Trans.*, 1809, 99, 446.

[100] *Crell's Annalen*, 1795, 2, 195, 310, 430.

[101] *Poggendorff's Annalen*, 1829, 16, 169.

[102] *J. prakt. Chem.*, 1842, 26, 478.

Later, Berthelot[103] found that ethylene passed through a tube heated to dull red heat was decomposed to ethane and acetylene. Marchand and Magnus[104] also detected the presence of methane in the product. DeWilde,[105] studying the effect of induced electric sparks on ethylene, obtained acetylene and hydrogen and later hydrogen and carbon.[106]

Day[107] circulated ethylene through a heated glass tube and found that decomposition accompanied by contraction in volume was noticeable at 350°-355° C., while polymerization was clearly indicated at 400°-408° C. At the latter temperature ethane and methane, but no hydrogen, were present in the reaction gas. In the same year Norton and Noyes[108] passed ethylene through a glass tube heated to a red heat and examined the products of reaction carefully. Carbon was deposited and benzene, naphthalene, and probably anthracene, were isolated from the liquid condensate. Only traces of acetylene were noted but from the bromination products of the reaction gas, propylene and butylene dibromide and butadiene tetrabromide were isolated. The formation of butadiene was assumed to occur according to the reaction:

$$2C_2H_4 \longrightarrow C_4H_6 + H_2$$

Bone and Coward[109] examined the decomposition of ethylene as well as that of other hydrocarbons. They circulated ethylene through a tube heated to 570°-580° C. for a period of 2½ hours and found that acetylene, ethane, methane, hydrogen, and aromatic hydrocarbons were produced and only a negligible amount of carbon was formed. At higher temperatures, methane, hydrogen, and carbon were the main products of reaction. It was concluded that acetylene was a principal product of the decomposition of ethylene. With ethylene and ethane it was supposed that the primary effect of high temperatures was to cause the elimination of hydrogen with simultaneous loosening, or dissolution, of the bond between the carbon atoms, labile residues such as $:CH_2$ and $\vdots CH$ being formed. These residues, assumed to possess a fugitive existence only, might subsequently either (a) form $H_2C{:}CH_2$ and $HC{:}CH$ by encounter between similar residues, or (b) break down directly into carbon and hydrogen, or (c) be directly hydrogenated to methane in an atmosphere already rich in hydrogen. For ethylene the scheme of decomposition is:

$$H_2C:CH_2 \longrightarrow 2(\vdots CH) + H_2 \longrightarrow \begin{array}{l} (a)\ C_2H_2 + H_2 \\ (b)\ 2C + 2H_2 \\ (c)\ + 2H_2 \longrightarrow \quad 2CH_4 \end{array}$$

Bone and Coward also stated that at comparatively low temperatures acetylene exhibits a strong tendency to polymerize to benzene, so that, whenever acetylene is a principal primary product of decomposition of another hydrocarbon (e.g., ethylene), there is always a marked secondary formation of aromatics at relatively low temperatures. Evidently, therefore, acetylene was regarded as an intermediate in the formation of aromatic hydrocarbons by pyrolysis.

Ipatiev[110] found that when ethylene was heated in an iron tube under high pressure, polymerization began at 325° C. and was rapid at 380°-400° C. The liquid products contained paraffin hydrocarbons from isopentane to nonane and cycloparaffins from nonanaphthene to pentadecanaphthene as well as amylene and hexylene. The fractions boiling above 250° C. were poorer in hydrogen so that evidently polymerization had been followed by other changes such as the splitting off of paraffins. Later, Ipatiev and Rutala[111] found that in the presence of anhydrous zinc chloride under a pressure of 70 atmospheres ethylene polymerized at 275° C. to various higher saturated and unsaturated aliphatic hydrocarbons together with various naphthenes.

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[103] *Ann. chim. phys.*, 1866, (4) 9, 442; *Ann.*, 1866, 139, 277.

[104] *Ann.*, 1853, 88, 349.

[105] *Bull. soc. chim.*, 1866, (2) 6, 267. *Z. für Chemie*, 1866, 735.

[106] See also Losanitsch and Jowitschitsch, *Ber.*, 1897, 30, 138; Jowitschitsch, *Monatshefte*, 1908, 29, 1, 5.

[107] *Amer. Chem. J.*, 1886, 8, 153; *Chem. Soc. Abs.*, 1886, 50, 781.

[108] *Amer. Chem. J.*, 1886, 8, 362.

[109] *J.C.S.*, 1908, 93, 1197.

[110] *Ber.*, 1911, 44, 2978.

Davidson,[112] as a result of an investigation of the thermal decomposition of the ethane-propane mixture of natural gas, assigned an important rôle to ethylene in the production of aromatic hydrocarbons. It was assumed that ethylene yielded butadiene, thus:

$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

The condensation of another molecule of ethylene with butadiene would yield cyclohexene which probably had no separate existence, but broke down to benzene and hydrogen. In 1922 Zanetti, Suydam and Offner[113] studied the effect of temperature on the yield of butadiene. A stream of ethylene was passed through a tube (material unstated) at a constant rate of 7.8 liters per hour (heating duration, 0.8 min.). The proportion of butadiene formed reached a maximum of 0.96 per cent of the ethylene supplied at 750° C., its formation beginning between 550° and 600° C. and dropping off between 850° and 900° C. The falling off in the production of butadiene above 750° C. is coincident with the beginning of the formation of aromatics. From this it was suggested that the formation of aromatic hydrocarbons from ethylene takes place, at least in part, through the intermediate formation of butadiene. Williams-Gardner[114] also recognized that ethylene is important in the formation of aromatic hydrocarbons from ethane at temperatures above 750° C.

Walker[115] studied the reactions of ethylene at temperatures between 100° and 600° C. in the presence of various catalysts. In Jena glass in the absence of a catalyst ethylene was stable at temperatures below 600° C. Silica, silica gel plus borax, silica plus lime, lime, borax, calcium silicate, and zinc oxide were found to be inert towards ethylene up to 600° C. but ethylene reduced ferric oxide (Fe_2O_3) completely at 500° C., zinc oxide at 800° to 900° C., and lead oxide at 600° C. At temperatures from 100° to 550° C. ethylene was partly polymerized by metallic sodium to a colorless oil with gradual production of sodium ethylene carbide. Nickel and iron promoted the formation of carbon, hydrogen, and methane.

The thermal decomposition of ethylene in the presence of silica was studied by Hague and Wheeler.[116] Samples of ethylene were heated at different temperatures in quartz bulbs for three hours and the resultant gases analyzed. Between 400° and 700° C. the ethylene was found to polymerize, yielding butylene, the optimum temperature being 500° C. The results are given in Table 17.

Several "stream" experiments were carried out at 600°, 650°, and 700° C. and the resulting gases brominated yielding butylene dibromide and butadiene tetrabromide. Liquid hydrocarbons, principally aromatic, were obtained at the higher temperatures, the optimum temperature for their production being 750°-800° C.

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[111] *Ber.*, 1913, **46**, 1748.
[112] *J. Ind. Eng. Chem.*, 1918, **10**, 901.
[113] *J.A.C.S.*, 1922, **44**, 2036.
[114] *Fuel*, 1925, **4**, 430.
[115] *J. Phys. Chem.*, 1927, **31**. 961.
[116] *J.C.S.*, 1929, 390.

TABLE 17.—*Effect of Heating Ethylene in Silica Bulbs for 3 Hours.*

	Analysis of Resulting Gas (per cent by volume)				
Temp. ° C.	Higher Olefins	C_2H_4	H_2	CH_4	C_2H_6
400	3.5	96.5	—	—	—
450	8.0	92.0	—	—	—
500	13.7	76.0	—	—	10.3
550	7.9	55.1	2.9	12.0	22.1
600	6.0	30.0	2.7	25.4	35.1
650	4.2	19.0	11.2	52.7	12.9
700	1.9	16.5	15.4	57.5	8.7
750	0.7	8.2	18.7	67.0	5.4

and the total yield at 800° C. representing 28.9 per cent of the ethylene passed. Table 18 shows the results of some stream experiments in silica tubes.

TABLE 18.—*Decomposition of Ethylene.*

				Gas Analyses (per cent by volume)			
Temp. ° C.	Total Liquids	Benzene Fraction	Higher Olefins	C_2H_2[a]	C_2H_4	H_2	CH_4
	——Per Cent——						
700	13.5	6.6	9.2	8.2	55.2	5.9	8.7
750	25.5	13.1	4.4	4.8	40.5	13.1	28.8
800	28.9	10.7	1.4	4.2	16.1	27.9	44.0
850	15.5	7.8	0.4	1.1	6.6	35.6	50.0

[a] These figures for the acetylene content were too high. On passing some of the reaction gas through ammoniacal silver chloride only traces of precipitate were formed.

From a study of the non-catalytic pyrolysis of ethylene at 450° to 600° C. at ordinary pressure, Pease[117] concluded that butylene is the first product of the reaction. The precise nature of the reaction is not clear but it is probable, according to Pease, that molecular excitation and chain reactions play important rôles. Later, he[118] made a study of the kinetics of the polymerization of ethylene at 2.5, 5, and 10 atmospheres pressure in the temperature range 350° to 500° C. It was found that at least 50 per cent of the ethylene may be polymerized to gaseous and liquid monolefins without the formation of more than a few per cent of hydrogen and saturated hydrocarbons. The polymerization reaction, which is probably homogeneous, was found to be approximately bimolecular and to have a temperature coefficient of 2.3 per 25° C., which is abnormally low for this type of change.

Some of the data from the previously mentioned work of Schneider and Frolich[119] on the cracking of ethylene in silica tubes at a pressure of 0.2 atmosphere are shown in Figure 10. These results indicate that at zero reaction there are formed for each 100 moles of ethylene reacting about 41 moles of hydrogen, 36 moles of butadiene, 12 moles of propylene and 3 moles of butylene. They also indicate that about 72 per cent of the ethylene reacting forms butadiene and hydrogen as initial products:

$$2C_2H_4 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2$$

Since a positive test for acetylene was always obtained, the excess of 5 moles of hydrogen may have come from a reaction producing acetylene. Ethane and methane were found to be definitely secondary products but it was observed that propylene was a primary pyrolytic product under the experimental conditions. This conclusion, though at first sight rather improbable, has been substantiated by the work of Lenher,[120] who found that propylene was the most important product of the polymerization of ethylene during the slow oxidation of ethylene with oxygen at temperatures of 450° to 520° C. A number of experiments with high ethylene concentrations and oxygen concentrations of about 5 per cent showed that below 520° C. propylene and butylene are the only hydrocarbons formed in oxygen-activated polymerizations. Thus, an experiment at 505° C. using a gas containing 87.0 per cent of ethylene and 8.8 per cent of oxygen and a time of reaction of 3.0 seconds, a 30.5 per cent yield of higher olefins was obtained. By careful analytical fractionation these were found to consist of 83 per cent of propylene and 14.6 per cent of butylene. A slow-oxidation experiment at 600° C. yielded a hydrocarbon product consisting of 59.3 per cent of propylene, 2.2 per cent of butylene, and 28.4 per cent of amylenes. In order to account for the formation of propylene as an initial product in the activated polymerization process Lenher advances three possible mechanisms (a) by intermolecular collision, (b) by the formation of an excited intermediate molecule C_4H_8' (not butylene) which then reacts with a further molecule of ethylene thus:

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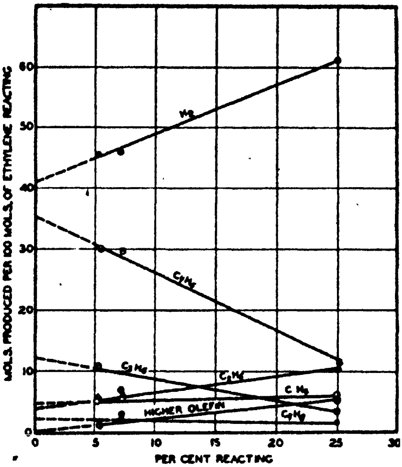
[117] *J.A.C.S.*, 1930, **52**, 1158.
[118] *J.A.C.S.*, 1931, **53**, 613; *Brit. Chem. Abs.* **B**, 1931, 436.
[119] *Ind. Eng. Chem.*, 1931, **23**, 1405.



Courtesy Industrial and Engineering Chemistry.

FIG. 10.—Pyrolysis of Ethylene (in Silica) at 725° C. and 0.2 Atmosphere. (Schneider and Frolich.)

$$2C_2H_4 \longrightarrow C_4H_8'$$
$$C_4H_8' + C_2H_4 \longrightarrow 2C_3H_6$$

and (c) the condensation of a free methylene radical with ethylene according to the scheme:

$$CH_2{=}CH_2 \longrightarrow 2(CH_2{=})$$
$$CH_2{=}CH_2 + (CH_2{=}) \longrightarrow CH_3CH{=}CH_2$$

Lenher considers that the last explanation is perhaps more probable than the others.

The production of liquid, mainly aromatic, hydrocarbons by the high temperature pyrolysis of ethylene has been studied by a number of workers including Smolenski,[121] Waterman and Tulleners,[122] Mailhe and Renaudie,[123] and Berl and Forst.[124] The last named employed a porcelain reaction tube at a temperature of 800° to 900° C. and obtained up to 43 per cent of liquid products containing aromatic hydrocarbons, benzene, naphthalene, and anthracene, as well as cyclopentadiene.

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[120] *J.A.C.S.*, 1931, 53, 3752.

[121] *Przemysl Chem.*, 1927, 11, 146; *Chem. Abs.*, 1929, 23, 2929.

[122] *Brennstoff-Chem.*, 1930, 11, 337; *Brit. Chem. Abs.* B, 1930, 975. *Cf. J. Inst. Pet. Tech.*, 1931, 17, 506; *Chem. Abs.*, 1932, 26, 308.

[123] *Compt. rend.*, 1930, 191, 265; *Chem. Abs.*, 1930, 24, 5283.

[124] *Z. angew. Chem.*, 1931, 44, 193; *Brit. Chem. Abs.* A, 1931, 596.

PROPYLENE

The pyrolysis of propylene in pyrex glass or quartz tubes at temperatures above 600° C. (below which temperature no change occurred even when the contact time was 50 seconds) was studied by Hurd and Meinert,[125] who concluded that the reaction was predominantly homogeneous and unimolecular. The products of pyrolysis consisted of hydrogen, methane, ethylene, and paraffin gases (chiefly ethane), while in certain experiments 20 to 25 per cent of the propylene was converted into a liquid of an aromatic nature. When pyrolyzed in monel metal tubes propylene was found to undergo profound decomposition even at temperatures as low as 350° C. and the products consisted largely of carbon and hydrogen. The reaction in monel metal tubes was found to be autocatalytic, the sooty carbon deposited on the walls of the tube at the beginning of the experiment accelerating the reaction so that it proceeded much more rapidly after 20 minutes.

Wheeler and Wood[126] studied the pyrolysis of propylene in a vertical quartz reaction tube at temperatures of 650° to 900° C. and found that liquid hydrocarbons could be obtained in yields as high as 40 per cent under certain conditions. The results of the experiments of these investigators are shown in Table 19.

TABLE 19.—*Pyrolysis of Propylene in Quartz Tubes.*

Temp.	650° C.	700° C.	750° C.	800° C.	850° C.	900° C.
Contact time, seconds	58.2	55	52.5	50	47.7	45.7
Yields (per cent by weight of propylene)						
Total liquids	5.2	20.3	35.6	40.6	33.8	11.9
Distillate up to 170° C.	3.2	12.9	20.4	19.0	14.6	6.8
Carbon	Nil	trace	trace	1.7	9.5	not determined
Analysis of Gaseous Products (per cent by volume)						
H_2	0.5	7.0	14.4	23.6	36.7	66.5
CH_4	2.1	18.9	49.1	70.7	85.9	86.1
C_2H_6	2.5	7.9	6.8	5.4	4.5	3.1
C_2H_4	7.7	23.5	37.0	28.1	18.6	8.0
C_3H_6	86.9	45.6	10.4	1.5	0.5	0.5
C_4H_8	4.1	6.5	2.0	0.5		
C_4H_6	0.2	0.6	0.4	0.3		

The lower-boiling liquids obtained from the decomposition at 650° C. were mainly monocyclic hydroaromatic hydrocarbons with one double bond in the ring, while those produced at 700° C. were mainly benzene and toluene. At higher temperatures more complex aromatic hydrocarbons predominated in the liquid products. Wheeler and Wood concluded that one of the most important primary reactions occurring in the pyrolysis of propylene was its decomposition into equal molecular proportions of ethylene and butylene according to the equation:

$$2C_3H_6 \longrightarrow C_2H_4 + C_4H_8.$$

The work of Schneider and Frolich[127] has shed much light on the nature of the primary reactions occurring in the pyrolysis of propylene in silica reaction tubes at 725° C. The experimental results obtained at 0.2 atmosphere pressure are shown in Figure 11, from which it will be seen that at zero reaction about 48 per cent of propylene is converted into ethylene and butylene according to

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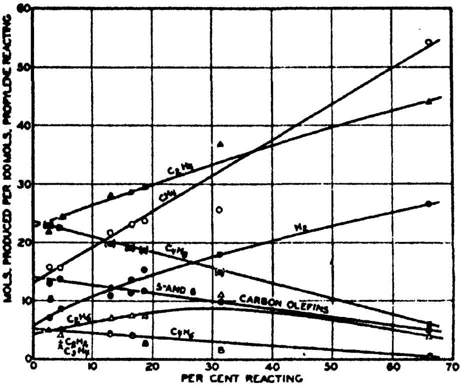
[125] *J.A.C.S.*, 1930, 52, 4978.
[126] *J.C.S.*, 1930, 1819.
[127] *Ind. Eng. Chem.*, 1931, 23, 1405.



Courtesy Industrial and Engineering Chemistry.

FIG. 11.—Pyrolysis of Propylene (in Silica) at 725° C. and 0.2 Atmosphere. (Schneider and Frolich.)

the above reaction, while about 10 per cent goes to form butadiene and ethane according to the reaction:

$$2C_3H_6 \longrightarrow C_2H_6 + C_4H_6$$

Hydrogen, methane, and unsaturated hydrocarbons containing five and six carbon atoms are also formed as primary products, apparently by such reactions as

$$2C_3H_6 \longrightarrow C_5H_8 + CH_4 \quad \text{and} \quad 2C_3H_6 \longrightarrow C_6H_{10} + H_2$$

In spite of the fact that the above mechanism would indicate that propylene undergoes bimolecular reactions during pyrolysis, Schneider and Frolich confirm the conclusion of previous workers that the cracking reactions behave approximately as first order homogeneous gas reactions.

The production of liquid hydrocarbons by pyrolysis of propylene in the presence of silica gel at 650° C. and 700° C. has been studied by Mailhe and Renaudie,[128] who found that the liquid condensate contained low-boiling olefins, benzene, toluene, and m-xylene, as well as more complicated polynuclear aromatic hydrocarbons.

Groll,[129] from a study of the pyrolytic conversion of ethylene, propylene, propane, n-butane, isobutane, and 2-butene at about 800° C., observed that propylene yielded the highest proportion of aromatic hydrocarbons. Diminished pressure and reaction time and lower temperature favor the formation of acetylene.

BUTYLENES

The pyrolysis of the two straight-chain isomers, 1-butene and 2-butene, in vertical silica reaction tubes and at atmospheric pressure has been studied by Wheeler and Wood.[130] The decomposition products of the two isomers were similar, though 2-butene was somewhat more stable than 1-butene.[131] Approximately equal volumes of methane and propylene were produced at 600° C., indicating that a probable primary reaction was the rupture of the terminal carbon-carbon bond, followed by hydrogenation of the radicals so formed. The hydrogen necessary for the latter process was believed to come from the simultaneous formation of butadiene according to the equation:

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[128] *Compt. rend.*, 1930, **191**, 851; *Brit. Chem. Abs.* **A**, 1931, 60.

[129] *Ind. Eng. Chem.*, 1933, **25**, 784; British Patent 369,351, 1930; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 2163.

[130] *J.C.S.*, 1930, 1819.

[131] To convert 1-butene to 2-butene, Runge and Mueller-Cunradi (U. S. Patent, 1,914,674, June 1933; assigned to I.G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4253) proposed heating at

$$C_4H_8 \longrightarrow C_4H_6 + H_2$$

Large quantities of liquid products were formed during the pyrolysis of these butenes, oil formation being at a maximum at about 750° C. The liquid products formed at lower temperatures (600° C.) contained large proportions of cyclohexene and cyclohexadiene hydrocarbons, particularly the former, but benzene and toluene were present in comparatively small amounts. At higher temperatures the liquid products were predominantly aromatic in character. The results of Wheeler and Wood on the pyrolysis of 1-butene and 2-butene are summarized in Table 20.

TABLE 20.—*Pyrolysis of 1-Butene and 2-Butene in Silica Tubes.*

Temp.	600° C.	650° C.	700° C.	750° C.	800° C.	850° C.	900° C.
Contact time, seconds	61.5	58.2	55	52.5	50	47.7	45.7
1-Butene							
Yields (per cent by weight of butene treated)							
Total liquids	12.9	29.8	35.8	39.6	39.4	35.0	13.9
Distillate up to 170° C.	6.5	20.3	23.6	22.4	19.9	16.2	7.8
Carbon	Nil	Nil	trace	trace	1.0	4.7	7.1
Gas Analysis (per cent by volume of butene treated)							
H_2	0.8	6.2	11.9	17.3	27.2	50.5	85.2
CH_4	8.1	37.2	62.1	78.5	89.0	95.7	103.3
C_2H_6	1.9	7.1	10.6	9.7	7.6	6.1	5.0
C_2H_4	3.2	14.2	22.3	31.4	30.2	20.6	9.6
C_3H_6	7.6	24.5	19.6	5.6	2.0	1.0	0.9
C_4H_8	54.1	19.8	2.1	1.3	1.0		
C_4H_6	0.9	1.7	1.4	0.2			
2-Butene							
Yields (per cent by weight of butene treated)							
Total liquids	5.2	27.0	37.0	39.6	37.9	31.6	12.4
Distillate up to 170° C.	1.4	17.2	25.8	23.2	18.6	14.2	6.1
Carbon	Nil	Nil	trace	trace	1.4	4.7	5.4
Gas Analysis (per cent by volume of butene treated)							
H_2	0.9	4.9	11.1	17.6	28.4	48.4	83.3
CH_4	2.8	31.4	62.0	76.5	90.0	96.1	103.1
C_2H_6	1.2	7.8	11.8	9.1	7.9	5.7	3.7
C_2H_4	1.3	8.9	19.8	27.9	24.4	16.9	8.3
C_3H_6	2.6	17.8	19.2	5.3	1.6	1.2	1.6
C_4H_8	65.0	20.0	2.6	2.1	0.5		
C_4H_6	0.8	1.7	0.9	0.4			

In the presence of silica gel at 650° to 700° C., 1-butene formed liquid unsaturated hydrocarbons and benzene, toluene and m-xylene, together with 40 per cent (by volume) each of propylene and methane, according to Mailhe and

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550° C. in an empty quartz tube or at 420° C. in contact with calcium oxide, aluminum phosphate on pumice or bauxite. Temperature has been shown to play two rôles in this isomerization: it changes the rate and permanently changes the power of the catalyst, according to Matignon, Moureu, and Dodé (*Compt. rend.*, 1933, **196**, 973, 1560; *Chem. Abs.*, 1933, **27**, 2934, 3910).

Renaudie.[132] 2-Butene at a higher temperature yielded somewhat more benzene and toluene in addition to naphthalene and anthracene.

A study of the pyrolysis of isobutylene was made by Hurd and Spence,[133] who subjected this hydrocarbon to thermal treatment in pyrex glass tubes at 600° to 700° C. Isobutylene was found to be much more stable thermally than isobutane and its decomposition was very slow at 600° C. In other respects, the reactions of these two hydrocarbons were also materially different. Isobutane decomposed initially into gaseous hydrocarbons of lower molecular weight, but isobutylene, on the contrary, gave higher molecular weight hydrocarbons. Thus, nearly half of the decomposed isobutylene was converted into liquid hydrocarbons, the remainder appearing as gaseous products. Table 21 gives some of the results of Hurd and Spence on isobutylene.

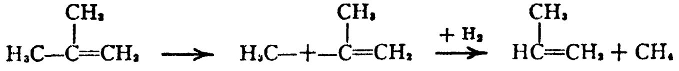
TABLE 21.—*Decomposition of Isobutylene in Pyrex Glass Tubes.*

			Cc. Gaseous Products per Liter Isobutylene Decomposed						Oil Yield
Temp. ° C.	Contact Time Sec.	% Decom-position	C_3H_6	CH_4	Iso-C_4H_{10}	H_2	C_2H_2	C_2H_4+ Aro-matics	% Iso-butylene Decom-posed
599	200	20	305	590	270	175	15	90	—
652	27	22.7	172	286	176	150	35	31	39.6
652	13	11.1	144	135	198	54	108	99	63
700	12	30.2	218	586	133	242	43	66	46.6
700	18	47.7	228	655	61	260	59	69	63

It is remarkable that no butadiene was found in the gaseous reaction products. An examination of the liquid products obtained at 700° C. showed that these consisted chiefly of aromatic hydrocarbons, benzene and toluene having been identified and the probable presence of xylene, naphthalene, anthracene, and phenanthrene indicated. The fraction boiling up to 76° C. gave evidence of containing appreciable amounts of unsaturated hydrocarbons. The decomposition of isobutylene was found to be homogeneous and unimolecular.

Hurd and Spence suggest, as the mechanism of the reaction, that heat may rupture the C—C or C—H bonds, and that it may activate the C=C double bond. The double bond is considered sufficiently strong to resist complete rupture, thereby creating a radical with two free bonds. Three such "activated" olefin molecules from isobutylene, that is, $(CH_3)_2\overset{|}{C}—\overset{|}{C}H_2$, would, by combination, produce a cyclohexane derivative, which, at the elevated temperature of formation, would be dehydrogenated into benzene derivatives.

It seems more than likely, however, that at least one of the reactions taking place in the thermal decomposition of isobutylene (judging from the production of propylene and methane) is the formation of free radicals (one of which is the methyl radical) followed by hydrogenation by the hydrogen derived from another phase of the process thus:



$$H_3C—\overset{\overset{CH_3}{|}}{C}=CH_2 \longrightarrow H_3C—+—\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{+H_2} H\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_4$$

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[132] *Ann. combustibles liquides,* 1931, 6, 79; *Chem. Zentr.,* 1931, 2, 1270; *Brit. Chem. Abs.* **A,** 1932, 250.

[133] *J.A.C.S.*, 1929, 51, 3561: the pyrolysis of isobutylene was also investigated by Noyes (*Mass. Inst. Technology Quarterly*, 1888, 1, 278), Nef, (*Ann.*, 1901, **318**, 24), Lebedev and Kobliansky (*Ber.*, 1930, **63**, 103, 1432), Ipatiev (*Ber.*, 1903, **36**, 2003), and by Ipatiev and Sdzitovecky (*J. Russ. Phys.-Chem. Soc.*, 1907, **39**, 897).

Pentenes

Of the pentenes studied, trimethylethylene appears to be the most stable and isopropylethylene the least so. Norris and Reuter[134] showed that isopropylethylene undergoes isomerization to trimethylethylene to the extent of 10 per cent when heated in a silica tube containing alumina for 16 seconds at 450° C. With a similar heating period, the isomerization was 29 per cent in the presence of phosphoric acid at 500° C., and 47 per cent in the presence of aluminum sulphate at 425° C. Under similar conditions neither trimethylethylene nor 2-pentene undergo any change. Previously, Ipatiev[135] reported that isopropylethylene is isomerized to trimethylethylene to the extent of about 80 per cent by exposure to silica at 500° to 505° C. or to alumina at 525° to 535° C.

The decomposition of 2-pentene in silica tubes at 600° C. was investigated by Norris and Reuter,[136] who obtained the following proportions of products in percentages by weight: 2-pentene, 33%; hydrocarbons of higher molecular weight, 15%; methane, 7.8%; butadiene, 8%; butylene, 8%; propylene, 4%; ethylene, 2%. Some carbon was deposited in the reaction tube but no free hydrogen was found among the products. In the mixture of hydrocarbons of molecular weights lower than 2-pentene, the components were present in the following approximate molecular ratio: methane, 100; butadiene, 27; propylene, 21; ethylene, 15.

An interpretation of these results is necessarily difficult on account of the complexity of the products but it is evident that polymerization, demethanation, and dehydrogenation proceed simultaneously. Since the number of molecules of methane was approximately equal to the number of molecules of other hydrocarbons present, loss of a methyl group can be assumed with subsequent hydrogenation of the unsaturated residues formed thus:

$$CH_3CH_2CH{=}CHCH_3 \longrightarrow CH_3CH_2CH{=}CH{-} + CH_3{-}$$
$$\xrightarrow{H_2} CH_3CH_2CH{=}CH_2 + CH_4$$

The hydrogen necessary for the latter process was presumably produced partly from decomposition of hydrocarbons with deposition of carbon and partly from the dehydrogenation of butylene to give butadiene thus:

$$CH_3CH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

Pyrolysis of 2-pentene in the presence of silica gel in a quartz tube at 670° C. was found by Mailhe and Renaudie[137] to yield a gas consisting of 52 per cent propylene and butylene, 34 per cent methane and 6 per cent hydrogen, together with oil and tar. At the same temperature isopropylethylene yielded 47 per cent ethylene homologues, 38 per cent methane, 7 per cent hydrogen, and oil and tar.

Norris and Reuter examined the pyrolysis of trimethylethylene at a temperature of 650° C. under conditions similar to those used with 2-pentene. As before, no free hydrogen was produced and the products of decomposition consisted of one-third higher molecular weight substances and two-thirds of substances of lower molecular weight with methane making up about 50 per cent of the gases formed. Here again, demethanation followed by hydrogenation of the residues would suffice to explain part of the decomposition process thus:

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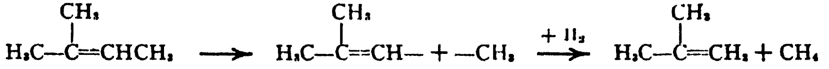
[134] *J.A.C.S.*, 1927, **49**, 2624.
[135] *Ber.*, 1903, **36**, 2003; *J. Russ. Phys.-Chem. Soc.*, 1902, **34**, 839.
[136] *Loc. cit.*
[137] *Compt. rend.*, 1931, **192**, 561; *Chem. Abs.*, 1931, **25**, 2682.



$$H_3C-\overset{CH_3}{\overset{|}{C}}=CHCH_3 \longrightarrow H_3C-\overset{CH_3}{\overset{|}{C}}=CH- + -CH_3 \xrightarrow{+H_2} H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_4$$

No 1,3-butadiene was observed in the reaction gas, which is in agreement with the theory since isobutylene could not be dehydrogenated to 1,3-butadiene without rearrangement.

Staudinger, Endle and Herold[138] studied the pyrolysis of trimethylethylene at 750° C. at atmospheric pressure and also under reduced pressure. Working at 15 mm. pressure, 50 grams of trimethylethylene yielded 8.3 grams of isoprene, 0.2 gram of butadiene and about 1.1 grams of ethylene together with some propylene. An earlier investigation of Haber and Oechelhäuser[139] on the pyrolysis of this amylene at temperatures from 600° to 1060° C. in porcelain tubes showed that at lower temperatures (750°-790° C.) the gaseous products consisted mainly of ethylene and methane. At higher temperatures (1050°-1060° C.) the gaseous products contained 50 per cent hydrogen, 30 per cent methane, and only 5 per cent ethylene, heavy aromatic tars being also formed.

Of considerable scientific interest is the work of Norris and Thomson,[140] who made a careful determination of the temperatures at which 1-pentene, 2-pentene, and trimethylethylene begin to decompose when heated in a Pyrex glass vessel for one hour. The observed initial cracking temperatures of 1-pentene, 2-pentene, and trimethylethylene were about 389° C., 400° C., and 433° C., respectively, while breaks in the curves at 420° C., 421° C., and 488° C., respectively, indicated that a second type of cracking reaction takes place at these temperatures. Above a certain temperature the rates of expansion of the heated vapors of each hydrocarbon either remained constant or decreased as the temperature was raised, indicating that both pyrolysis and polymerization reactions were then taking place. It was found that a trace of moisture doubled the rate of cracking of 2-pentene at temperatures just above the initial cracking temperature, which was not, however, altered by such addition of water vapor.

Higher Olefins

Hurd and Bollman[141] studied the pyrolysis of diallyl, 4-methyl-1-pentene, allylcyclohexane, and 4-phenyl-1-butene. In contrast to propylene and isobutylene,[142] which require temperatures of 700° C. or above for extensive decomposition, these olefins decomposed considerably in the range of 425° to 500° C. A predominating proportion of propylene with no allene and only a small proportion of ethylene was formed. In every case high-boiling polymerization products were also encountered. Hurd and Bollman explain these facts by assuming that α-olefins undergo a preliminary scission into radicals at the allyl bond:

$$R-C_3H_5 \longrightarrow R- + C_3H_5-$$

These radicals then acquire hydrogen atoms from some source, presumably largely from the original hydrocarbon, and escape as RH + C_3H_6. The dehydrogenated material may undergo polymerization, in common with the original unsaturated hydrocarbon. From this work they conclude that simple scission into two compounds (such as that of n-butane into ethane and ethylene or methane and propylene) should not be considered the primary effect, even though each of them may be found in the reaction products.

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[138] *Ber.*, 1913, 46, 2466.
[139] *J. Gasbel.*, 1896, 39, 799, 805, 813, 830. Haber, *Ber.*, 1896, 29, 2691.
[140] *J.A.C.S.*, 1931, 53, 3108.
[141] *J.A.C.S.*, 1933, 55, 699.
[142] Hurd and Spence, *J.A.C.S.*, 1929, 51, 3561; and Hurd and Meinert, *J.A.C.S.*, 1930, 52, 4978; previously mentioned in this chapter.

Hugel and Szayna[143] studied the pyrolysis of a mixture of straight-chain octenes (consisting essentially of 40 per cent 1-octene and 60 per cent 2-octene) in quartz tubes over the temperature range 290° C. to 600° C. The lowest temperature at which any change was detected was about 365° C. where the reaction products had a wider boiling range (117° to 130° C.) than the initial material (boiling range 121.5° to 124° C.), though no appreciable evolution of gas occurred. This effect was presumed to be due to isomerization of the straight-chain octenes to branched-chain isomers of lower boiling points.[144] Above 400° C., part of the octene decomposed with production of gas and a low-boiling liquid as well as some tar and carbon. The low-boiling liquid produced at 440° C. showed indications of the presence of unsaturated cyclic hydrocarbons while that obtained by pyrolysis at 540° C. and 600° C. contained benzene. The composition of the gaseous products of cracking at various temperatures is summarized in Table 22.

TABLE 22.—*Gaseous Products of Pyrolysis of Octene in Silica Tubes.*

Temp. ° C.	Gas Produced in Moles per Mole of Octene Decomposed	Gas Analysis (per cent by volume) Paraffins	Olefins	Acetylenes (?)	H_2
438°-444° C.	1.01	87	8.5	—	4.5
480°-490°	1.54	73	17.5	3	6.5
540°-549°	2.63	69	19.5	5	6.5
600°	2.70	67	15	4.5	13.5

A comprehensive examination of the thermal decomposition of hexadecene at atmospheric, and also at superatmospheric pressures, has been made by Gault and his collaborators.[145] Hexadecene, prepared by the distillation of cetyl palmitate under diminished pressure, was subjected to pyrolysis in the absence of catalysts at temperatures of 350° to 725° C. The gaseous products of cracking contained a maximum of 66 to 68 per cent unsaturated hydrocarbons at 575° to 600° C., this optimum production of unsaturated gases being coincident with a minimum (about 26 per cent) content of saturated gaseous hydrocarbons. As the temperature of the decomposition was raised the proportion of saturated gaseous hydrocarbons increased, that of unsaturated gases diminished, and the yield of hydrogen, which appeared at the beginning of the pyrolysis, increased with rising temperature. Ethylene, propylene, butylene, amylene, and butadiene were identified in the gaseous products of cracking by means of their bromine addition compounds. The proportion of butadiene in the gaseous products varied from 4 per cent to 7 per cent and reached a maximum at about 500° C., being equal at this temperature to about 1 per cent of the original hexadecene. At 600° C. and over, some carbon was deposited and aromatic hydrocarbons began to preponderate in the liquid products. It was considered by these investigators

[143] *Ann. combustibles liquides,* 1926, 1, 781.

[144] Numerous cases of the isomerization of monolefins under the influence of heat have been reported, especially in the presence of catalysts. Among the higher monolefins, 2,6-dimethyl-7-octene has been shown to be completely isomerized to 2,6-dimethyl-6-octene in the presence of palladized asbestos at 200° C. in the vapor phase (Zelinsky and Levina, *Ber.,* 1929, **62**, 1861.

[145] Gault and Altchidjian, *Compt. rend.,* 1924, **178**, 2092; *Ann. chim.,* 1924, (10) **2**, 209; Gault, Hessel and Altchidjian, *Compt. rend.,* 1924, **178**, 1562.

that the main steps in the pyrolysis of hexadecene at atmospheric pressure consisted in the splitting off of methane from the ends of the hexadecene molecule, the olefinic residues thus formed subsequently undergoing further disintegration into smaller fragments. Hugel and Goldthorpe[146] showed that, in the presence of nickel-impregnated pumice at 350° C., hexadecene undergoes rapid decomposition with a copious production of free carbon. A similar result was obtained using iron-pumice catalyst at 425° C., although with pumice alone carbon deposition was first noticeable at 500° C.

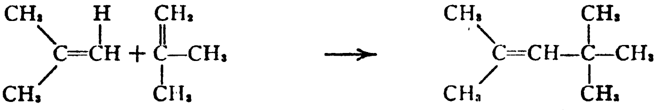
Pyrolysis of Olefins Under Pressure

Before leaving the subject of the thermal decomposition of the olefins, reference must be made to work carried out on the effect of heating olefins under pressure. In this connection the work of Ipatiev on the high pressure condensation of ethylene at temperatures above 325° C. has already been discussed.

Ipatiev[147] also studied the effect of heating isobutylene in a closed tube at 380° to 390° C. The gaseous products consisted of 10.8 per cent hydrogen, 69.6 per cent C_nH_{2n} hydrocarbons, and 20.1 per cent C_nH_{2n+2} hydrocarbons. The oil obtained from 500 grams of isobutylene distilled as follows:

° C.	Grams	° C.	Grams
23–100	70	215–260	82
100–150	105	260–280	55
150–190	55	Over 280	60
190–215	58		

Paraffins and olefins were present in the lower-boiling fractions and cycloparaffins as well as olefins and hydrocarbons deficient in hydrogen were found in the higher fractions. No aromatic hydrocarbons were identified. It would appear that polymerization of the olefin to di- and tri-isobutylene and higher polymers occurs first, followed by decomposition and cyclicization of the polymers. The first stage of the polymerization reaction may probably be written:



Diisobutylene

Engler and Rutala[148] studied the effect of heating amylene in a sealed tube. Heating at 230° C. for eleven days raised the specific gravity from 0.6647 to 0.6725 and halved the bromine absorption, and heating for twelve days at 300° C. raised the specific gravity from 0.6647 to 0.7505. By heating 350 grams of commercial amylene for 32 days at 325° C. ten liters of permanent gas containing 10 per cent of hydrogen, 1.5 per cent of hydrocarbons having the formula C_nH_{2n}, and 91.1 per cent of hydrocarbons having the formula C_nH_{2n+2}, were produced as well as a liquid having a bluish-green fluorescence and a terpene-like odor. The higher-boiling fractions were rich in olefin hydrocarbons, which were removed from the oil by fuming sulphuric acid. The resulting olefin-free oil was fractionated, and the following hydrocarbons were shown to be present: pentanes, hexanes, heptanes, cyclohexane, methylcyclopentane, heptanaphthene, octane, octanaphthene, nonanaphthene, decanaphthene, undecanaphthene, dodecanaphthene, tetradecanaphthene, pentadecanaphthene, and higher-boiling cycloparaffins (as well as hydrocarbons more deficient in hydrogen in the highest-boiling fractions).

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[146] *Ann. combustibles liquides*, 1928, 3, 613.
[147] *Ber.*, 1911, 44, 2978.
[148] *Ber.*, 1909, 42, 4620.

Engler and Eberle[149] heated a hexylene (consisting of a mixture of 1-, 2-, and 3-hexenes;[149a] b.p. 67°-68° C.; d_{15}^{15} 0.687) for 14 days in a sealed tube at 360° to 365° C. The product boiled between 67° C. and 240° C. and had a lower bromine absorption (especially in the higher fractions) than the original hexylene. Low-boiling paraffins and cycloparaffins, such as cyclohexane and dodecanaphthene, were present and the higher fractions were poorer in hydrogen than a substance of the formula C_nH_{2n}. It was concluded that besides polymerization of the hexylene to higher olefins, cyclicization to cycloparaffins and subsequent decomposition of the higher polymers to substances both richer (i.e., paraffins) and poorer in hydrogen had taken place.

A comprehensive study[150] of the reactions induced by heating hexadecene under pressure at a temperature of about 300° C. showed that polymerization to higher monolefins, $C_{32}H_{64}$ and $C_{48}H_{96}$, was the predominant process especially in the absence of a gaseous phase. As might be expected, the polymerization reactions were greatly accelerated by higher pressures and a study of the process as a function of time indicated that it was probably an equilibrium dependent upon the pressure and temperature.

The effect of heat and pressure on a vapor phase cracked gasoline has been investigated by Payne and Lowy.[151] The gasoline was produced by cracking a light solar oil at 600° C. under a pressure of 100 pounds per square inch for 10 minutes. Some of the gasoline distillate so obtained was heated at 300° C. under 68 atmospheres pressure for 6 hours in a steel bomb. Analyses of the original and heat-treated distillates indicated that not only had a decrease in the percentage of olefin hydrocarbons been effected, but also an increase in the percentage of naphthenes. (See Table 23.)

TABLE 23.—*Effect of Heat and Pressure on Vapor Phase Cracked Gasoline.*

	Original Distillate to 201.5° C.	Treated Distillate to 201.5° C.
	Per Cent	
Olefins	35.0	24.5
Aromatics	17.0	15.5
Naphthenes	25.9	34.2
Paraffins	22.1	25.8

Both the original and heat-treated gasolines were distilled and fractions taken approximately every 5.5° C., up to 201.5° C., and the fractions analyzed. It was observed that heat treatment had decreased the percentage of unsaturated hydrocarbons in the various fractions but had increased the percentage of naphthenes. Polymerization was thought to be responsible for the larger proportion of the distillate boiling above 201.5° C. after the heat treatment as well as for the disappearance of cycloalkenes and the formation of hydrocarbons containing hydrogen atoms easily replaceable by halogens (as indicated by the Johansen iodine substitution value).

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[149] *Petroleum,* 1907, **2**, 915; *Z. angew. Chem.,* 1908, **2**, 1589; Engler and Rutala, *Ber.,* 1909, **42**, 4628.

[149a] *Cf.* Welt, *Ber.,* 1897, **30**, 1494; Michael and Hartmann, *Ber.,* 1906, **39**, 2150.

[150] Hugel and Cohn, *J. Inst. Pet. Tech.,* 1929, **15**, 744; *Chimie et industrie,* Special No., March 1930, 201; *Chem. Abs.,* 1930, **24**, 5714; *Ann. combustibles liquides,* 1932, **7**, 15; *Chem. Abs.,* 1932, **26**, 4299; Hugel, *Trans. 2nd World Power Conf., (Berlin),* 1930, **8**, 56; *Chem. Abs.,* 1932, **26**, 2853; *J. Inst. Pet. Tech.,* 1930, **16**, 390A.

[151] *Ind. Eng. Chem.,* 1932, **24**, 432.

DIOLEFINS

The thermal behavior of the diolefin hydrocarbons has been but little studied. In the past, attention has largely been concentrated on the polymerization of conjugated diolefins under the influence of heat, with or without catalysts, to liquid, resinous, and rubber-like polymers (see Chapter 26). Cyclic unsaturated dimers (polymers of two molecules of the original substance) are principally obtained by heating these diolefins alone in sealed tubes at temperatures below 300° C. Little has been reported on the pyrolysis of non-conjugated diolefins. The thermal decomposition of both conjugated and non-conjugated diolefins deserves much more attention, since the former, particularly 1,3-butadiene, seem to be important in the production of aromatic from aliphatic hydrocarbons.

Staudinger, Endle and Herold[152] examined the pyrolytic decomposition of isoprene, butadiene, and 2,3-dimethyl-1,3-butadiene. It was found that isoprene was partly polymerized at 400°-500° C., yielding terpene-like products together with amylene. Between 600° and 700° C. complete decomposition occurred and ethylene, propylene, and butadiene were present in the gaseous products. Above 700° C. aromatic hydrocarbons appeared and at 750° C. and 800° C. aromatic hydrocarbons were formed almost exclusively. Thus, at 750° C. isoprene yielded 44 to 55 per cent of a tar closely resembling coal tar and containing benzene, toluene, naphthalene, anthracene, and higher aromatics. The gaseous products contained butadiene, hydrogen, methane and ethylene, and carbon was deposited in the reaction chamber.

Butadiene at 750° C. gave a mixture of aromatic hydrocarbons. At 800° C., using a quartz tube packed with coke, butadiene produced benzene, saturated liquid hydrocarbons, naphthalene, and anthracene. Similarly, 2,3-dimethylbutadiene at 800° C. yielded aromatic hydrocarbons.

SUMMARY OF THERMAL REACTIONS OF OLEFIN HYDROCARBONS

Our knowledge of the mechanism of the thermal reactions of the olefin hydrocarbons is exceedingly scanty and only the simplest member, namely ethylene, has been examined in any detail. It appears, however, that the olefins are sharply differentiated from the corresponding paraffin hydrocarbons by the fact that, whereas the latter decompose initially with the production of substances of lower molecular weight only, the olefins tend to produce, partly at any rate, quantities of higher molecular weight hydrocarbons, and at the same time some decomposition to lower molecular weight substances also takes place.[152a] Olefin hydrocarbons, in general, are more rapidly decomposed than paraffins, this difference becoming less, however, with increasing molecular weight of the compounds.[153]

The synthesis of higher hydrocarbons from olefins by pyrolysis probably occurs in the first place by a simple polymerization to produce a higher olefin. Thus, ethylene yields butylene, and isobutylene, diisobutylene. The polymerized olefin can, however, undergo decomposition in several ways so that the reaction products tend to become complex. The polymerization of olefins to produce higher olefins is possible thermodynamically up to 500° C. as has been shown by Sachanen and Tilicheyev.[154] There is no doubt that this process affords an explanation of the production of larger molecules from olefins in thermal decomposition. The application of pressure tends naturally to favor polymerization, as confirmed by the work of Ipatiev and others.

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[152] *Ber.*, 1913, **46**, 2466.

[152a] Hurd (*Ind. Eng. Chem.*, 1934, **26**, 50) reviewed the work on pyrolysis of unsaturated hydrocarbons and placed the reaction products into the groups: Simple products with lower boiling points than the original substances, isomers and dehydrogenation products in the same distillation range as the original hydrocarbons, and polymers with higher boiling points than the original substance. He stated that contact time is more important than size of tube or rate of flow of the gas through the tube in pyrolysis.

[153] Tilicheyev and Feigin, *Rept. Conf. Cracking Hydrog. Grozni*, 1931, 1, 267; *Brit. Chem. Abs.* **B**, 1932, 456; *Chem. Abs.*, 1932, **26**, 1105.

The polymers so formed might be expected to be monolefins having molecular weights which are simple multiples of that of the parent material. There is much evidence in support of this supposition, particularly in thermal reactions carried out under pressure and at moderate temperatures, e.g., the thermal treatment of hexadecene at 300° C. under pressure yields monolefinic polymers of the type $(C_{16}H_{32})x$, where x is a simple whole number. In the high-temperature pyrolysis of the simple monolefins such as ethylene, it has usually been assumed that thermal polymerization gives rise initially to polymers of this type. Certain work, however, particularly that of Schneider and Frolich, and also of Lenher, appears to indicate that reactions of the type

$$3C_2H_4 \longrightarrow 2C_3H_6,$$

e.g., the transformation of ethylene to propylene and not to butylene, can take place. The mechanism of such reactions is still very obscure.

Though polymerization reactions are essentially favored by low temperatures and the presence of catalysts, they play an important rôle in the pyrolysis of olefins even at elevated temperatures and in the absence of catalysts.

Isomerization of olefins to five- and six-membered cycloparaffins is possible thermodynamically up to about 500° C., though Sachanen and Tilicheyev consider that in commercial cracking operations the velocity of this reaction is too small to yield appreciable quantities of cycloparaffins. In the presence of catalysts, however, such as aluminum chloride, this isomerization can undoubtedly take place.

Besides polymerization to higher olefins and isomerization to cycloparaffins, the olefin can also, in part, undergo decomposition with the production of lower hydrocarbons. The exact mode of scission is doubtful but this can probably take place in several ways. Thus, an olefin molecule can break down to form two lower olefins (a change analogous to depolymerization) or a paraffin hydrocarbon can be split off and a diolefin produced. By the first reaction amylene would yield ethylene and propylene, while by the second, methane and butadiene would result thus:

$$(1)\ CH_3CH_2CH_2CH{=}CH_2 \longrightarrow CH_3CH{=}CH_2 + CH_2{=}CH_2$$
$$(2)\ CH_3CH_2CH_2CH{=}CH_2 \longrightarrow CH_4 + CH_2{=}CHCH{=}CH_2$$

The primary reactions in the thermal decomposition of olefins may then be considered to be:

(1) Polymerization to higher olefins.
(2) Decomposition with the production of lower olefins, paraffins, and diolefins.

It appears from the work of Schneider and Frolich that some of the primary reactions of the olefins are much more complicated than was hitherto believed. For example, the most important primary reaction occurring in the non-catalytic pyrolysis of ethylene at 725° C. is one in which butadiene and hydrogen are formed (apparently without the intermediate production of butylene), according to the equation:

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[154] *Ber.*, 1929, 62, 658.

$$2C_2H_4 \longrightarrow C_4H_6 + H_2$$

It should be pointed out, however, that the formation of butylene as a transitory intermediate product in this reaction is not entirely disproved by the work of Schneider and Frolich and that at lower temperatures the reaction given above may be found to consist of two consecutive reactions; namely, polymerization to butylene and subsequent dehydrogenation of the butylene. Certainly it is difficult to visualize the exact mechanism of the change as written in the above equation.

Finally an initial stage in the pyrolysis of olefins may be isomerization to a more stable unsaturated hydrocarbon. As the temperature rises the primary pyrolytic reactions, which are different for individual olefins, are obscured by secondary changes which appear to be the same for almost all olefins. These secondary reactions yield aromatic hydrocarbons and hydrogen. Hague and Wheeler and a number of prior workers consider that aromatic hydrocarbons are produced from olefins through the formation of butadiene. Thus, ethylene by polymerization gives butylene which loses hydrogen and is converted into butadiene. A continuation of this process suffices to yield hexatriene, which can be supposed to yield benzene by loss of hydrogen.

THERMAL DECOMPOSITION OF ACETYLENE

The pyrolysis of acetylene is of importance in the study of the thermal reactions of hydrocarbons especially from the point of view of the importance assigned to it as an intermediate product by various workers, more especially by Berthelot, who regarded acetylene as the fundamental source of all synthetic processes during pyrolysis. The great importance assigned to acetylene in the building up of larger molecules during pyrolysis has been to some extent discounted by later research, which has directed attention to the important functions of the olefins and diolefins. Nevertheless, it appears that acetylene is, in some cases, to be regarded as a source of the aromatic hydrocarbons formed during pyrolysis, especially from the decomposition of methane at very high temperatures. Acetylene is of great interest also on account of the fact that its stability at very high temperatures is greater than that of any other volatile hydrocarbon. Thermodynamic calculations indicate that acetylene cannot be formed in any amount in the pyrolysis of hydrocarbons at temperatures below 850° C.

Bone and Coward[155] showed that at 500° C. and 600° C. the non-catalytic thermal decomposition of acetylene resulted mainly in formation of polymers and to a lesser extent in decomposition into its elements. Reactions of less importance are hydrogenation to ethylene, ethane, and methane. At higher temperatures polymerization occurs to a minor extent and decomposition into carbon and hydrogen and production of methane predominates. The most favorable temperature range for condensation of acetylene is 600° to 700° C.

The pyrolysis of acetylene to produce higher hydrocarbons (principally aromatic) has been noticed by a large number of investigators, particularly by Meyer and his co-workers,[156] who isolated the following hydrocarbons from the products of pyrolysis: hexene, benzene, toluene, o-, m-, and p-xylenes, styrene, pseudocumene, mesitylene, indene, hydrindene, naphthalene, hydronaphthalene,

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[155] *J.C.S.*, 1908, 93, 1197.

[156] *Ber.*, 1912, 45, 1609; 1913, 46, 3183; 1914, 47, 2765; 1917, 50, 422; 1918, 51, 1571.

1- and 2-methylnaphthalenes, 1,4-dimethylnaphthalene, diphenyl, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthrene, pyrene, and chrysene.

Zelinsky[157] obtained a yield of 76 to 80 per cent of tar calculated on the weight of acetylene used by passing acetylene over activated wood charcoal at 640°-650° C. Benzene was found to be the most important constituent of the tar, and toluene and xylene were present in smaller amounts. About 35 per cent of the tar was benzene, 4 per cent toluene, 6.7 per cent naphthalene, 1 per cent fluorene and anthracene, and 0.4 per cent p-xylene, styrene, and indene.

The polymerization of acetylene has been investigated by Fischer, Bangert and Pichler.[158] They found that on passing acetylene over activated charcoal or silica gel at 600°-700° C., hydrogen, methane, and carbon are formed. The carbon which was thus deposited acted as a polymerization catalyst, the proportion of liquid hydrocarbons increasing until about 70 per cent of the acetylene was converted to light and heavy oils. The light oil (boiling up to 150° C.) contained 70 per cent aromatic and 30 per cent unsaturated hydrocarbons. The exhausted catalyst could be regenerated by the addition of carbon dioxide to the acetylene, this admixture also serving to increase the production of light oil. Low pressures did not increase the efficiency of the process.

According to Pease,[159] in the pyrolysis of acetylene, polymerization is the only reaction of importance at temperatures up to 600° C. The reaction is homogeneous and bimolecular and is retarded by packing the reaction tube with glass. Schläpfer and Brunner[160] concluded that the thermal polymerization of acetylene in glass tubes, which begins at 300° C. but does not become rapid until a temperature of 450° C. is attained, is homogeneous and probably bimolecular. Increased glass surface has little effect on the reaction velocity, but copper accelerates and iron powder or carbon retards the rate of polymerization. Fukagawa[160a] found that, in the presence of reduced nickel, the temperature of maximum thermal polymerization rises with repeated use of the catalyst and that the optimum temperature was below 300° C.

The polymerization of acetylene to benzene is an exothermic process and the reaction is, therefore, likely to become a spontaneously explosive decomposition. In order to control the reaction to form aromatic hydrocarbons, Berl and Hoffman[161] used carbon dioxide as a diluent for absorbing the heat and obtained a 98 per cent yield of liquid products using a carbon catalyst at 600°-700° C. Iron, silica, and acid or alkaline contact masses (e.g., tin or calcium oxides) were unfavorable to the production of liquid products but the yield of the latter was improved by charging the gas with water vapor.

The thermal reactions of acetylene may be summarized as follows: At temperatures up to 700° C. the main reaction is that of condensation to liquid and solid hydrocarbons, mostly aromatics, and decomposition into its elements is of secondary importance. At higher temperatures the polymerization reaction is suppressed and the formation of carbon and hydrogen predominates. At very high temperatures, however, acetylene becomes more stable with respect to decomposition.

PYROLYSIS OF NON-AROMATIC CYCLIC HYDROCARBONS

Hydrocarbons possessing a closed ring of carbon atoms but lacking the peculiar properties of aromatic compounds are known as cycloparaffins, polymethylenes and naphthenes. The latter term is loosely used, however, to designate all cyclic hydrocarbons (other than aromatics), more particularly those found in various petroleum fractions. Various polynuclear naphthenes are known but their modes of decomposition on pyrolysis have been little investigated. The term cycloparaffins, which indicates their cyclic saturated character, is perhaps preferable and will be used to designate hydrocarbons of this class.

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[157] *Compt. rend.*, 1923, **177**, 882.
[158] *Brennstoff-Chem.*, 1929, **10**, 279.
[159] *J.A.C.S.*, 1929, **51**, 3470.
[160] *Helv. Chim. Acta*, 1930, 13, 1125; *Chem. Abs.*, 1931, **25**, 1726.
[160a] *J. Chem. Soc. Japan*, 1929, **50**, 689; *Chem. Abs.*, 1931, **25**, 5613.
[161] *Z. angew. Chem.*, 1931, **44**, 259.

Calculations of the stability of monocyclic saturated hydrocarbons on the basis of the Baeyer strain theory indicate that five- and six-membered carbon ring systems (and particularly the former) should be the most stable. In agreement with this, it has been found that cyclopentane and cyclohexane derivatives predominate among the naphthene hydrocarbons of crude petroleum. Chemical evidence in the main is in agreement with Baeyer's theory, thus ring systems containing 2, 3, 4, 7 or 9 carbon atoms being rather unstable, and those containing 5 and 6 carbons are relatively stable. Yet Ruzicka[162] has shown that systems containing 10 to 30 carbons are surprisingly stable. Furthermore, the naturally occurring compound, civetone (the active odorous principal in civet) is an unsaturated cyclic ketone with 17 carbon atoms, hydrogenation of which yielded dihydrocivetone which proved to be identical with cycloheptadecanone synthesized by Ruzicka.

The tendency of cyclohexane derivatives to lose hydrogen at fairly low temperatures in the presence of catalysts and form principally benzene derivatives was first demonstrated by Sabatier and Senderens.[163] Cyclohexane in the presence of nickel at 270°-280° C. was found to yield benzene but some methane was also formed. Substituted cyclohexanes and hydronaphthalenes behaved in a similar way. Reduced copper was somewhat less active as a catalyst in promoting this change, dehydrogenation of cyclohexane beginning at 300° C.

CYCLOPROPANE, CYCLOBUTANE AND CYCLOPENTANE

Cycloparaffins with rings of less than 5 carbon atoms appear to isomerize partly into the corresponding olefin under the influence of heat. Thus Tanatar[164] reported that when trimethylene (cyclopropane) was passed slowly through a glass tube heated to a dull red heat, it was converted to propylene. At 100° C. in the presence of platinum black a 40 per cent conversion was obtained.

Ipatiev and Huhn[165] observed very little isomerization of cyclopropane when the gas was passed slowly through a heated glass tube without a catalyst. At 200° C. in the presence of platinum sponge a 5 per cent conversion was noted, and at 315° C., 29 per cent conversion was obtained. When an aluminum oxide catalyst was used at a temperature of 370°-385° C., a 20 per cent conversion to propylene took place. 1,1-Dimethylcyclopropane passed over an aluminum oxide catalyst at 340°-345° C. was almost completely converted to trimethylethylene.

The isomerization of methylcyclopropane to 2-butene and isobutylene has been reported by Dojarenko,[166] and that of ethylcyclopropane to methylethylethylene by Rozanov.[167] In both instances aluminum oxide was used as the catalyst.

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[162] *Chem. Weekblad*, 1928, **25**, 614; *Chem. Abs.*, 1929, **23**, 1906; *Helv. Chim. Acta*, 1926, **9**, 230; *Chem. Abs.*, 1926, **20**, 1791; *Helv. Chim. Acta*, 1926, **9**, 715; *Chem. Abs.*, 1927, **21**, 571; Ruzicka, Brugger, Pfeiffer, Schinz and Stoll, *Helv. Chim. Acta*, 1926, **9**, 499; *Chem. Abs.*, 1926, **20**, 2151; Ruzicka, Stoll and Schinz, *Helv. Chim. Acta*, 1928, **11**, 670; *Chem. Abs.*, 1928, **22**, 4482; *Helv. Chim. Acta*, 1928, **11**, 1174; *Chem. Abs.*, 1929, **23**, 1111; Ruzicka, Brugger, Seidel and Schinz, *Helv. Chim. Acta*, 1928, **11**, 496; *Chem. Abs.*, 1928, **22**, 2928.

[163] *Compt. rend.*, 1897, **124**, 616.

[164] *Ber.*, 1896, **29**, 1297. Also *Z. physik. Chem.*, 1902, **41**, 735.

[165] *Ber.*, 1903, **36**, 2014.

[166] *Ber.*, 1926, **59**, 2933.

[167] *J. Russ. Phys.-Chem. Soc.*, 1916, **48**, 168; *Chem. Abs.*, 1917, **11**, 454.

Trautz and Winkler[168] studied the kinetics of this isomerization and found it to be a unimolecular reaction. At high temperatures (700° C.) and with long times of contact, however, the formation of secondary products, hydrogen and methane, from propylene takes place. Methylenecyclopropane[169] is said to yield 1,3-butadiene when passed over aluminum oxide at 350° C.

The pyrolysis of cyclobutane apparently has not been recorded. Rozanov,[170] however, reported that methylcyclobutane is isomerized by contact with alumina at 350°-400° C. yielding a mixture of pentenes and their polymers.

Fillipov[171] observed the isomerization of methylenecyclobutane to methylcyclobutene in the presence of aluminum oxide at 300° C. At somewhat higher temperatures (395° to 430° C.) with this same catalyst, Dojarenko[172] found methylenecyclobutene to be converted into p-cymene, isoprene, hydrocarbons having the formula C_8H_{10}, and gaseous products.

Cyclopentane is the most stable of the cyclic saturated hydrocarbons, and its purely pyrolytic decomposition has not yet been reported. Some of its derivatives, however, have been dehydrogenated in the presence of substances known to be specifically dehydrogenating catalysts. For example, cyclohexylcyclopentane when passed at 300° C. over platinum deposited on charcoal yields phenylcyclopentane.[173]

CYCLOHEXANE

Jones[174] conducted an investigation on the thermal decompositions of cyclohexane, methylcyclohexane, and di- and tetra-hydronaphthalenes. The experiments were carried out in a glass bulb filled with broken porcelain and heated to 520° C. The decomposition of dihydronaphthalene began at 390° C. and that of the other three hydrocarbons started at 490° to 510° C. An analysis of the resulting gases showed the presence of large proportions of hydrogen, in contrast to the behavior of the higher paraffin hydrocarbons on pyrolysis. The gas from cyclohexane contained over 40 per cent of hydrogen and also olefins, benzene, methane, and ethane, the presence of the latter constituents indicating that, besides simple dehydrogenation, scission of a C—C bond had taken place. The liquid products from cyclohexane were found to contain benzene. The hydronaphthalenes decomposed with the production of much naphthalene, the gaseous products containing over 80 per cent of hydrogen. Jones concluded that the hydrocarbons studied tended, in general, to retain their ring structures.

Frolich, Simard and White,[175] investigating the formation of butadiene by the cracking of hydrocarbons, observed that at 654° C. cyclohexane yielded this diolefin to the extent of 20.6 per cent based on the cyclohexane decomposed. A calcium aluminate catalyst has been used for the decomposition of cyclohexane into ethylene and butadiene at 600° C.[176]

Ipatiev and Dowgelewitsch[177] studied the reactions of cyclohexane under the influence of heat with and without pressure and also in the presence of aluminum oxide, and found that this hydrocarbon is considerably more stable than hexane. At ordinary pressure and at a temperature of 750° C. the gaseous products from the decomposition contained hydrogen, 14.0 per cent; olefins, 44.5 per cent; and saturated hydrocarbons, 42.0 per cent. The liquid products contained unchanged cyclohexane, small amounts of olefins, and other hydrocarbons which did not react with a nitrating acid mixture nor with potassium permanganate. Under a pressure of 100 to 110 atmospheres the reaction was much more violent and at 510° C. the liquid products contained olefins (5 to 10 per cent), aromatic hydrocarbons, and cycloparaffins including methylcyclopentane. The isomerization of cyclohexane to methylcyclopentane took place under the influence of heat only at high pressure. In the presence of various catalysts, however, this isomerization takes place at ordinary pressure and at lower temperatures.

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[168] *J. prakt. Chem.*, 1922, (2) 104, 53.

[169] Merezhkovskii, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 2072; *Chem. Abs.*, 1915, 9, 799.

[170] *J. Russ. Phys.-Chem. Soc.*, 1929, 61, 2291; *Chem. Abs.*, 1930, 24, 3763.

[171] *J. Russ. Phys.-Chem. Soc.*, 1914, 46, 1141; *Chem. Abs.*, 1915, 9, 1904.

[172] *Loc. cit.*

[173] Zelinsky and Titz, *Ber.*, 1931, 64, 183; *Chem. Abs.*, 1931, 25, 2981.

[174] *J.C.S.*, 1915, 107, 1582.

[175] *Ind. Eng. Chem.*, 1930, 22, 240.

[176] I. G. Farbenindustrie A.-G., British Patent 297,398, 1927; *Brit. Chem. Abs.* B, 1928, 884.

[177] *Ber.*, 1911, 44, 2987.

In the presence of silica gel, cyclohexane begins to decompose at 600° and cyclohexene at about 550° C., according to Mailhe.[178] The products indicated that cyclohexane is dehydrogenated to cyclohexene, which is subsequently converted to benzene and to hexene. Further degradation yields a series of olefins in which propylene predominates. Above 700° C. pyrolytic condensation to benzene, toluene, xylene, naphthalene, anthracene and more complex hydrocarbons occurs.

The dehydrogenation of cyclohexane in the presence of palladium black was found by Zelinsky and his collaborators[179] to be a reversible process. At 100° to 110° C. benzene was readily hydrogenated in its presence and the dehydrogenation of cyclohexane to benzene began at 170° C., attaining a maximum velocity at 300° C. Under similar conditions methylcyclohexane yielded toluene and hydrogen. Hexane, cyclopentane and methylcyclopentane were not affected so that this might constitute a method for isolating cyclopentane derivatives in the presence of cyclohexanes.

Nickel, palladium and platinum were found by Zelinsky to be dehydrogenating catalysts at temperatures of 150° C. to 408° C. Of these three, nickel was the poorest. Platinum and palladium black also appear in some cases to exhibit selective dehydrogenating action. Thus, when a mixture of cyclohexane and methylcyclohexane was passed over the catalyst, only the cyclohexane was converted to hydrogen and benzene while the methylcyclohexane remained unchanged. Other cyclohexane derivatives, hexahydrocymene and hexahydroxylene, were dehydrogenated by platinum black at 300° to 310° C. to yield the corresponding aromatic compounds, cymene and xylene. Zelinsky was of the opinion that in the dehydrogenation process all six hydrogen atoms were eliminated simultaneously, without the intermediate formation of either the di- or tetra-hydroaromatic compounds.

Methylenecyclohexane remained unaltered when heated with quinoline, but in the presence of a mixture of quinoline and quinoline hydriodide at 145° C., it was isomerized to 1-methylcyclohexene. The same change was brought about at 150° to 170° C. in the presence of benzoic acid.[180]

Cyclohexene when passed over palladium black at 92° C. yielded benzene and cyclohexane.[181] On heating in a bomb for 24 hours at 400° to 440° C. in the presence of aluminum oxide the products were hydrogen, gaseous saturated hydrocarbon bases, benzene and higher aromatic compounds.[182] 1,4-Dimethyl-3-cyclohexene at 140° C. in the presence of a palladium catalyst yielded principally dimethylcyclohexane. Toluene and methylcyclohexane were obtained from methylenecyclohexane at 116° to 118° C. in the presence of this same catalyst.[183]

The pyrolysis of allylcyclohexane, which has been studied by Hurd and

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[178] *Chimie et Industrie*, 1933, 29, 759; *Chem. Abs.*, 1933, 27, 3200.

[179] *Ber.*, 1911, 44, 3121; 1912, 45, 3679; 1923, 56, 787, 1249; 1924, 57, 667.

[180] Faworsky and Borgmann, *Ber.*, 1907, 40, 4863.

[181] Zelinsky and Pawlow, *Ber.*, 1924, 57, 1066.

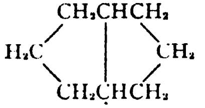
[182] Petrov, *J. Russ. Phys.-Chem. Soc.*, 1928, 60, 1435; *Chem. Abs.*, 1929, 23, 4453.

[183] Zelinsky, *Ber.*, 1924, 57, 2055.

Bollman,[184] yields a predominating proportion of propylene and the liquid products consist of cyclohexane, benzene and cyclohexene, together with tars and high-boiling material.

CYCLOHEPTANE AND HIGHER CYCLOPARAFFINS

The purely thermal decomposition of cycloheptane has not been reported. Willstätter and Kametaka,[185] however, have shown that in the presence of nickel and hydrogen at 235° C. this hydrocarbon is converted to methylcyclohexane and dimethylcyclopentane. Under similar conditions, but at a temperature of 205° to 210° C., cyclooctane yielded dimethylcyclohexane together with some other hydrocarbons which were apparently alkylated cyclopentanes. Zelinsky and Freimann[186] reported that at 300° C. in the presence of a platinum catalyst cyclooctane is converted to methylcycloheptane and bicyclo-(0,3,3)-octane, the formula of which is



PYROLYSIS OF PETROLEUM DISTILLATES

The pyrolysis of petroleum distillates, principally from naphthene-base stocks has been reported by several investigators. Ogloblin[187] obtained benzene, toluene, naphthalene and other aromatic compounds by a two-stage process. In the first stage the naphtha distillate (from Russian petroleum) was passed through an iron retort heated to 525° to 550° C., and the product was obtained in three fractions: (1) gas, (2) liquid boiling below 200° C., and (3) liquid boiling above 200° C. The portion boiling below 200° C. was decomposed at temperatures of from 700° C. to 1200° C. under 2 atmospheres pressure. The product obtained by this second stage was fractionated and the fraction boiling up to 120° C. was called "gray benzol." This "gray benzol," amounting to about 12 per cent of the petroleum, contained benzene, toluene and xylene. Fraction 3 from the first stage, boiling above 200° C., can be used for the production of naphthalene, anthracene, and similar hydrocarbons.

The pyrolysis of naphthenic petroleum hydrocarbons has been reported by Engler and Rosner,[188] by Egloff, Twomey and Moore,[189] and by Leslie.[190] The most interesting feature of the experiments of Leslie was the production of large proportions of unsaturated compounds when a naphthene-base oil was thermally treated under conditions which bring about primary chemical change without extensive secondary reactions.

SUMMARY OF THERMAL REACTIONS OF NON-AROMATIC CYCLIC HYDROCARBONS

Far too little careful experimental work on the pyrolysis of the cycloparaffin hydrocarbons has been reported for any far-reaching generalization to be made concerning the mechanism of the process. Undoubtedly, however, cyclopentane and cyclohexane derivatives are the most stable, even more so than the corresponding paraffins. Cycloparaffins with less than 5 carbon atoms in their ring have a tendency to isomerize to the corresponding olefin when heated. The cyclohexanes tend to isomerize to the corresponding methylcyclopentanes under the influence of heat and pressure and this reaction can probably be effected at lower temperatures by certain catalysts, such as aluminum chloride. Hydrogen iodide has been also used to effect similar isomerizations of cycloheptane.

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[184] *J.A.C.S.*, 1933, **55**, 699. See preceding section of this chapter on the thermal decomposition of olefins.

[185] *Ber.*, 1908, **41**, 1480.

[186] *Ber.*, 1930, **63**, 1485.

[187] *Z. Farben- u. Textil Chem.*, 1904, **3**, 293; *J.S.C.I.*, 1904, **23**, 931.

[188] *Chem. Rev. d. Fett. und Harz. Ind.*, 1906, **13**, 144.

[189] *Chem. Met. Eng.*, 1916, **15**, 387.

[190] "Motor Fuels, Their Production and Technology," Chemical Catalog Co., Inc., New York, 1923, 285.

In the presence of catalysts such as nickel, platinum and palladium black, cyclohexane derivatives tend to dehydrogenate with the production of benzene derivatives but cyclopentanes resist dehydrogenation, according to Zelinsky. The indications are that cyclohexane derivatives undergo non-catalytic thermal decomposition at temperatures above 500° C. to yield aromatic hydrocarbons and hydrogen, but from cyclohexane itself Jones obtained a notable production of olefin and paraffin hydrocarbons of lower molecular weight. The mechanism of this latter process, which would appear to involve a scission of a C—C bond in the ring itself, is still very obscure and much more experimental work is needed to clarify it. In cycloparaffin derivatives containing one or more alkyl groups substituted for hydrogen atoms, it is reasonable to suppose that the paraffinic side-chains will react analogously to the paraffins but this supposition requires experimental verification. A very careful study of the non-catalytic thermal decomposition of cyclopentane and its derivatives would be extremely valuable.

Balandin[191] has developed a theory of dehydrogenation catalysis, based upon the same idea underlying the "space theory" of catalysis advanced by Langmuir, Adkins and Burk, of interest here. Catalytic dehydrogenation occurs, according to this theory, when a group of surface atoms appropriately spaced and of the necessary activity absorb the reactant in a definitely oriented position. Because simultaneous action on the part of several surface atoms is postulated the theory is called the "multiple-hypothesis." Catalysts such as platinum, palladium, iridium, rhodium, copper, cobalt, nickel, iron, zinc, osmium or ruthenium are active because they possess structures fulfilling this condition.

Other predictions made from this theory are:

(1) Cyclopentane and cycloheptane, containing 5- and 7-membered rings, respectively, should not be dehydrogenated by metallic catalysts.

(2) Cyclohexene and cyclohexadiene should not be obtained as partial catalytic dehydrogenation products of cyclohexane.

(3) Di-substituted cyclohexanes should not be dehydrogenated when the substituted groups are on the same carbon atom.

The calculations by Sachanen and Tilicheyev[192] of the equilibrium constants of a number of hydrocarbon reactions at 477° C. show that the naphthenes tend to be dehydrogenated to benzene derivatives and that side chains can split off with the formation of olefins. The naphthenes as a class are intermediate between paraffins and aromatics as regards their stability to heat.

THERMAL DECOMPOSITION OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons as a class are more stable thermally than all other types of hydrocarbons and constitute the main product of the thermal decomposition of all other hydrocarbons at high temperatures. For example, aromatic hydrocarbons occur largely in the tar produced by the high-temperature carbonization of bituminous coal and also in the tar produced by the high-temperature cracking of liquid, solid, and gaseous hydrocarbons.

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[191] *Z. phys. Chem., Abt. B*, 1929, **2**, 289; *Chem. Abs.*, 1929, **23**, 2872.

[192] *Loc. cit.*

The first important work on the pyrolysis of aromatic hydrocarbons was conducted by Berthelot,[193] who passed various hydrocarbons through a porcelain tube heated to dull redness. Under these conditions benzene gave diphenyl, chrysene, and a resinous substance but no anthracene or naphthalene. Toluene yielded benzene, naphthalene, anthracene, and other hydrocarbons. Xylene gave toluene as a principal product, also benzene, naphthalene, and anthracene. Cumene yielded toluene and xylene in large quantities as well as benzene, naphthalene, anthracene, and chrysene. Later, Anschütz [194] concluded that many of the complex hydrocarbons produced during pyrolysis are formed by condensation with elimination of hydrogen thus:

$$2C_7H_8 \longrightarrow C_{14}H_{10} + 3H_2.$$

Smith and Lewcock [195] studied the decomposition of benzene in an iron tube and found that the chief product was diphenyl and that the amount of product boiling above 260° C. was small. At 600° C. no diphenyl was formed and 800° C. was found too high for optimum yields. Up to 70 per cent yields of diphenyl were obtained and it was observed that the presence of easily reduced oxides or of coke in the reaction tube favored the production of diphenyl.

Rittman and his co-workers [196] studied the reactions of benzene, xylene, toluene, naphthalene, and anthracene at various temperatures and pressures. The xylenes gave toluene, benzene, naphthalene, and anthracene. Toluene yielded benzene, anthracene, and naphthalene. Benzene yielded only naphthalene and anthracene whereas naphthalene formed anthracene but no other aromatic compound. Later, Zanetti and Egloff [197] found that the chief product of the decomposition of benzene at temperatures of 500° to 800° C. were diphenyl, diphenylbenzenes, carbon, and permanent gas. The formation of diphenyl began at 500° C. and was at a maximum at 750° C. Contrary to the results of Rittman and his collaborators, no naphthalene was formed. The permanent gas consisted of hydrogen saturated with benzene vapor and no acetylene was present. The formation of diphenyl was not favored by any catalyst but the decomposition of benzene into carbon and hydrogen was accelerated by the presence of iron and nickel.

Dufton and Cobb [198] demonstrated that in a stream of nitrogen rich in benzene, decomposition begins at about 550° C., with the production of diphenyl. The yield of diphenyl increases with increasing temperature to a maximum but at more elevated temperatures further decomposition sets in and a three-ring compound, diphenylbenzene, is formed. Toluene at temperatures of 600° C. and above yielded ditolyl together with stilbene, naphthalene, anthracene, and other substances. Several other investigators have shown that diphenyl can be produced from benzene at temperatures between 500° and 1000° C., the optimum temperature being 750° C., and this material is now being produced on a large scale by thermal processes (see Chapter 4).

The pyrolytic decomposition of benzene, toluene, and xylene, heated separately in an atmosphere of hydrogen, at a temperature of 500° C., and at pressures up to 270 atmospheres has been reported by Oda.[199] Benzene was the most stable of

[193] *Bull. soc. chim.*, 1867, (2), 7, 217.

[194] *Ber.*, 1878, 11, 1213.

[195] *J.C.S.*, 1912, 101, 1453.

[196] *Ind. Eng. Chem.*, 1915, 7, 1019; *Chem. Met. Eng.*, 1916, 14, 15.

[197] *Ind. Eng. Chem.*, 1917, 9, 350.

[198] *Gas-J.*, 1920, 150, 588.

[199] *J. Soc. Chem. Ind., Japan*, 1931, 34, 142B; *Brit. Chem. Abs.* A, 1931, 832.

the three, yielding some methane and about 1 to 2 per cent diphenyl. Toluene was decomposed more readily, yielding benzene and a mixture of hydrocarbons which were probably derivatives of diphenyl. Xylene yielded benzene, toluene and a complex mixture of liquid and solid hydrocarbons, the solid ones appearing to be anthracene derivatives.

Hurd and Bollman[200] isolated naphthalene, toluene (and some benzene) together with propylene from the products of the pyrolysis of 4-phenyl-1-butene.

The work of Sachanen and Tilicheyev[201] on the decomposition of naphthalene and other aromatic hydrocarbons is of great interest. On heating naphthalene for 4 hours at 475° C. no carbon was formed and a dinaphthyl was isolated in the reaction products. Anthracene, heated to the same temperature for 2½ hours, yielded gaseous products and changed into a coke-like material, 60 per cent of which was insoluble in benzene.

Since fluorene[202] is produced by passing diphenylmethane through red-hot tubes, its presence in tars is probably due to similar pyrogenetic reactions. The production of styrene by passing a mixture of benzene and ethylene through red-hot tubes is another example of these thermal reactions.[203] By this method Berthelot[204] was able to produce acenaphthene from naphthalene and ethylene and phenanthrene from diphenyl and ethylene. The formation of picene (1,2,7,8-dibenzophenanthrene, found in the residues from the distillation of crude petroleum by Graebe and Walter[205]) and similar hydrocarbons deficient in hydrogen[206] can, no doubt, be attributed to pyrolytic reactions.

SUMMARY OF THERMAL DECOMPOSITION OF AROMATIC HYDROCARBONS

The aromatic hydrocarbons tend to decompose into benzene or its immediate homologues and these then undergo a characteristic reaction, two nuclei coalescing to form a substance of higher molecular weight and hydrogen being simultaneously liberated. Thus, benzene forms diphenyl and hydrogen by the latter process. The polynuclear aromatic hydrocarbons, such as naphthalene, may also condense similarly with loss of hydrogen. A repetition of this process many times suffices to give coke-like substances of low hydrogen content. In this way, aromatics are probably to be regarded as the principal source of coke and heavy residuum in cracking reactions. From pure hydrocarbons no tar or coke is formed at moderate cracking temperatures or with comparatively short times of cracking.

Sachanen and Tilicheyev have calculated the equilibrium constants of various hydrocarbon reactions at 477° C. from thermal data by the aid of the Nernst formula and have arrived at the following conclusions in regard to the pyrolysis of aromatic hydrocarbons. Of the substituted aromatic hydrocarbons, the methyl-substituted benzenes, and to a lesser extent the ethyl-substituted ones, are the more resistant to heat. On the other hand, the benzene homologues with longer side chains tend to decompose more readily, the result being a splitting off of the side chains with the formation of either olefins or paraffins. Of the latter reactions the formation of styrene proceeds most easily.

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[200] *J.A.C.S.*, 1933, **55**, 699. See preceding section of this chapter on the thermal decomposition of olefins.

[201] *Ber.*, 1929, **62B**, 658.

[202] Graebe, *Ann.*, 1874, **174**, 194.

[203] Berthelot, *Ann.*, 1867, **142**, 257.

[204] *Bull. soc. chim.*, 1867, (2) **7**, 283; *ibid.*, 1867, (2) **8**, 247; *Ann. chim. et phys.*, 1867, (4) **12**, 226; *Chem. Zentr.*, 1867, 714.

[205] *Ber.*, 1881, **14**, 175.

[206] See Petroleum Coke, in Chapter 7.

Some conclusions of Pease and Morton,[207] arrived at in a study of the kinetics of dissociation of typical hydrocarbon vapors, are of interest in a broad general way. At 600° C. the order of stability of the hydrocarbons investigated was o-xylene, toluene, benzene, m-xylene, ethylbenzene, cyclohexane, 2-pentene, ethylcyclohexane, n-heptane. The dissociations appear to be normal, first-order, homogeneous gas reactions. The higher members of a series dissociate somewhat more rapidly at lower temperatures than the lower members. A side-chain on the benzene ring has nearly the same properties as the paraffin of the same number of carbon atoms. The cyclohexane ring is less stable than the benzene ring. On reaction, it first probably yields a smaller cycloparaffin ring.

[207] *J.A.C.S.*, 1933, 55, 3190.

Chapter 3

Cracking Processes and Their Products

In the previous chapter the pyrolytic reactions of a number of individual hydrocarbons, representatives of certain chemical types, have been discussed and an attempt has been made to distinguish the various stages in the resulting complex series of reactions. In the present chapter a description will be given of the salient features of the commercial cracking processes which have for their main object the production of an optimum amount of high-grade motor fuel from the higher-boiling fractions of petroleum. In a discussion of this character it is not necessary to enter into great detail regarding the type of plant used or the operating conditions except in so far as they affect the yield and kind of products. From the viewpoint of the chemist, the greatest interest is centered around the gaseous and low-boiling liquid products of commercial cracking operations which, on account of their content of lower olefins and other reactive hydrocarbons, are rapidly becoming the raw materials of a great organic chemical industry. In particular the gaseous products of cracking, though heretofore regarded by the refiner as undesirable by-products of value only as gaseous fuels, are a potential source of very large quantities of the simple unsaturated hydrocarbons, especially ethylene and propylene, the ready availability of which is already exerting a tremendous influence on the development of industrial aliphatic syntheses.[1]

Industrial cracking operations are concerned almost exclusively with the conversion of petroleum oils of higher boiling range than gasoline into low-boiling liquids of the gasoline type. It is true that high temperature pyrolysis was utilized during the World War for the production of aromatic hydrocarbons from petroleum fractions and at the present time there are indications of developments in the pyrolysis of natural gases for the production of the lower olefins and of aromatic oils. Compared, however, with the extent and importance of the great cracking industry for the production of motor fuels from higher petroleum fractions, all other phases of pyrolysis are at the moment quite negligible from a commercial standpoint.

The development of the commercial cracking art has been phenomenal, especially during the last decade. Despite the continued overproduction of crude oil and the decreased production of straight-run gasoline and natural-gas gasoline in the United States, cracked gasoline production in this country increased from 394,000 barrels daily in 1929 to 432,000 barrels in 1930, and again in 1931 to 488,000 barrels.[1a] Besides greatly increasing the yield of gasoline obtainable from crude petroleum, the cracking operation is capable of furnishing gasolines of much better anti-knock value than straight-run products. With an increasing demand for gasoline of higher octane number the cracking process has become of paramount importance, and its flexibility has been so increased that not only kerosene, gas oil, fuel oil, and even crude oils are being cracked to motor fuel, but also straight-run gasoline, especially heavy naphtha, is being subjected to a certain degree of cracking to improve its anti-knock value.[1b] The figures in Table 24, which show the cracked gasoline production in the United States, expressed as percentages of the annual total gasoline produced in this country, clearly reveal the growth of the cracking industry.[2]

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[1] See for example, Bowen, *Oil and Gas J.*, 1932, **30** (46), 88. Migey (*Refiner*, 1932, **11**, 547; *Brit. Chem. Abs.* B, 1933, 691) points out that cracking gas is an economical source of ethylene (98 per cent pure and sulphur free) which may be employed in the manufacture of metastyrene. Ellis (U. S. Patent 1,935,469, Nov. 14, 1933; assigned to Ellis-Foster Co.) suggests that after the removal of olefins the residual cracking gas be converted to hydrogen, which can then be used for catalytic hydrogenation operations. See also Egloff, *Ind. Eng. Chem.*, 1934, **26**, 41. The development of the oil cracking art is described by Keith and Montgomery, *Ind. Eng. Chem.*, 1934, **26**, 190.

[1a] Egloff, "Reports on the Progress of Naphthology," *J. Inst. Pet. Tech.*, 1932, **18**, 282.

TABLE 24.—*Percentage of Cracked Gasoline to Total Gasoline in the United States.*

Year	Per Cent	Year	Per Cent
1904	10.3	1923	31.0
1909	10.7	1924	33.0
1914	18.0	1925	34.9
1917	21.5	1926	37.7
1921	27.1	1927	40.0
1922	29.6	1928	41.0
		1930	43.0

Although the cracking of higher petroleum fractions for gasoline has been developed almost exclusively in the United States, a notable increase in cracking has taken place in certain other countries where the tariff position is such that crude oil can be profitably cracked after importation. This is particularly true of Italy.

Chemical Reactions Occurring during Cracking

The commercial cracking of petroleum hydrocarbons for gasoline is carried out at temperatures within the range of 400° to 650° C., and at atmospheric or higher pressures, depending upon the type of process employed. So-called vapor phase processes are operated at comparatively high temperatures and comparatively low pressures (usually atmospheric or slightly above atmospheric pressure), while those termed liquid phase processes necessitate the use of pressures up to 1000 pounds per square inch or higher in conjunction with a somewhat lower range of temperature, generally below 500° C. It is naturally impossible to set a definite temperature as the limit between liquid and vapor phase cracking operations, since this temperature will vary with conditions of pressure and also with the charging stock.[3] The hydrocarbon material to be cracked may be any petroleum fraction boiling above a medium gasoline range, though the gas oil fraction (the latter being the cut intermediate between the kerosene and lubricating oil fractions) is the usual cracking stock.[3a] In some instances "reduced" and "topped" crudes are used.[4] In the following discussion of the reactions involved in cracking operations attention is concentrated on the temperature range of 400° to 650° C., representing the limits of commercial operations at the present time.

[1b] Bataafsche Petroleum Maatschappij, French Patent 746,481, 1933; *Chem. Abs.*, 1933, **27**, 4665.

[2] Graetz, *Chim. et. ind.*, 1930, **24**, 271.

[3] The terms *liquid* and *vapor phase* were apparently used in early cracking developments to differentiate those processes operating at temperatures of about 400°-450° C. (750°-850° F.) and increased pressures from those employing higher temperatures, about 540° C. (1000° F.) and atmospheric or reduced pressures. Sometimes operations in which the charging stock passes into or through the cracking zone in the form of a mist or fog are erroneously designated vapor phase processes. In this connection compare Sachanen and Tilicheyev ("Chemistry and Technology of Cracking," The Chemical Catalog Co., Inc., 1932, 15), who, referring to McKee and Parker (*Ind. Eng. Chem.*, 1928, **20**, 1169), stated "it is entirely possible that these heavier components are also present in the state of an emulsion or as a fog, and that these non-homogeneous systems may be fairly stable."

[3a] From experiments on cracking Ragusa crude, Mariotti (*L'Ind. Chimica*, 1933, **8**, 4, 162; *Brit. Chem. Abs.* **B**, 1933, 338) concluded the best results were obtained with a fraction having a density of 0.91 to 0.92, and boiling between 186° and 360° C. Trusty (*Refiner*, 1932, **11**, 335; *Brit. Chem. Abs.* **B**, 1932, 968) considered the three criteria of a good cracking stock are: distillation range, carbon residue or tar number, and aniline point. An ideal cracking stock is a heavy closely fractionated gas oil, possessing a low carbon residue, and low aniline point.

The complete cracking process consists of a complex series of chemical reactions involving both decomposition and polymerization, the nature of the ultimate products being determined mainly by the character of the charging stock, the temperature and pressure of cracking and the time of exposure to cracking conditions.[5] Although a few of the primary cracking reactions exhibit a quasi-reversibility (for example, the dehydrogenation of paraffins to olefins and of cyclohexanes to benzene hydrocarbons and also, possibly, the polymerization and depolymerization of some olefins), most of the cracking reactions are of an irreversible character, the ultimate stable condition being in all probability the well-known methane-hydrogen-carbon equilibrium.

An insight can be gained into the various stages of the sequence of cracking reactions by the application of thermodynamics to the problem and also by a study of the primary cracking reactions of pure hydrocarbons. A knowledge of the free energy relationships of hydrocarbons enables us to predict whether a certain type of reaction is at all possible and also which of several competitive processes is the most likely to occur under any given conditions. On the other hand, thermodynamic calculations can tell us nothing of the rates at which reactions can proceed and, unfortunately, the transformations taking place in the cracking of petroleum are very largely controlled by the relative reaction rates. In order, therefore, to obtain a complete picture of such a complex sequence of processes it is necessary to consider not only the relative thermodynamic stabilities of various hydrocarbon types but also to correlate these with the results of experience in practical cracking operations and the experimental evidence obtained in the pyrolysis of pure hydrocarbons.

Thermodynamic Considerations

The thermodynamics of the thermal decomposition of various hydrocarbon types has been investigated theoretically by Francis and Kleinschmidt[6] on the basis of free energy calculations. Their results are best summarized by the graphs shown in Figure 12, in which the free energy per carbon atom of the formation of a number of hydrocarbons from their elements has been plotted against the temperature. Although, strictly speaking, one should compare the changes in free energy when starting with a definite weight of each of the two elements involved, a certain simplification is possible because of the fact that the carbon-hydrogen weight ratio is little different for various hydrocarbons over a considerable range. It will be seen from the curves that the free energies of formation (from their elements) of all hydrocarbons with the single exception of acetylene (and possibly the higher acetylenes) increase with rising temperature. Since the thermodynamic tendency at any temperature is from a higher to a lower line in the figure, it is obvious that all hydrocarbons tend to become increasingly unstable with respect to their elements with rising temperature, with the single exception of acetylene, which tends to become more stable at higher temperatures. It will be noticed also that the angles of slope of the curves for various hydrocarbons vary considerably and accordingly intersect one another. This indicates that the relative stabilities of different types of hydrocarbons are altered as the temperature rises. Thus, at temperatures below about 700° C. the ethylene curve lies above that of ethane, indicating that the tendency is towards hydrogenation in this lower range of temperatures, while at higher temperatures ethylene becomes more stable than ethane, i.e., the dehydrogenation reaction is favored. Because of the difference in the slope of the lines for the several olefin hydrocarbons they intersect at about 425° C., indicating that there is a tendency to polymerize below this temperature and to crack above this temperature. Other important conclusions which may be deduced from this series of curves can be summarized as follows:

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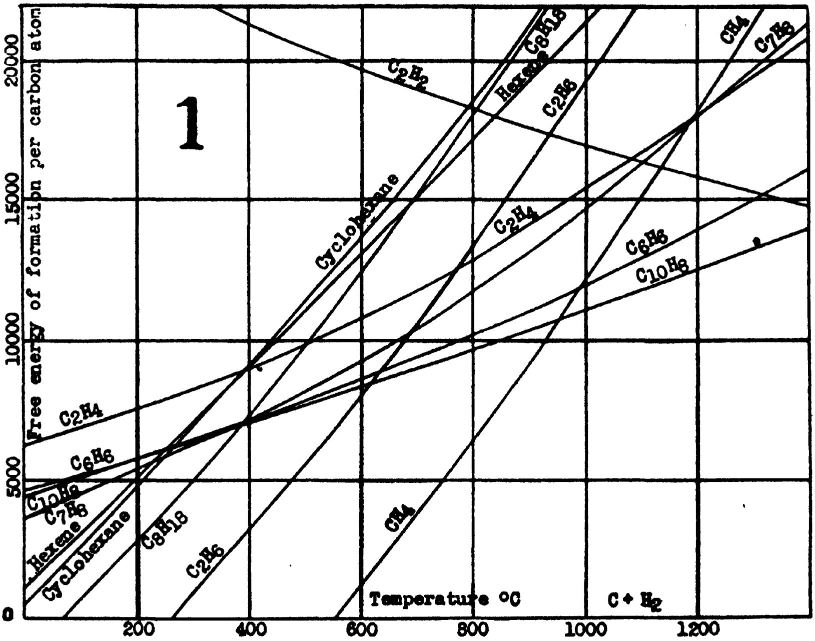
[4] "Reduced crudes" refer to crude oils from which the gasoline, kerosene and some gas oil have been removed by distillation. "Topped crudes" are those from which gasoline or gasoline and kerosene fractions have been taken off.

[5] For a review of the theory and mechanism of cracking, see Berl and Lind, *Petroleum Z.*, 1930, **26**, 1027, 1057; Mayer, *Petroleum Z.*, 1930, **26**, 1248; Graetz, *Chim. et ind.*, 1930, **24**, 271, 526; Petrov and Andreiev, *Ber.*, 1931, **64**, 1827; Sachanen and Tilicheyev, *Paliva a Topeni*, 1929, **11**, 94; *Chem. Abs.*, 1930, **24**, 4924; Bourgault, *Arts et métiers*, 1933, 169; *Chem. Abs.*, 1933, **27**, 3808; Fester, *Anal. Asoc. Quim. Argentina*, 1933, **21**, 24; *Brit. Chem. Abs.* **B**, 1933, 738; Wilson, *Proc. Roy. Soc.*, (*London*), 1927, **116A**, 501; 1929, **124A**, 16; 1933, **140A**, 1.

[6] *Oil and Gas J.*, 1929, **28**, 118; *Am. Petroleum Inst., Proc. 10th Ann. Meeting* **11**, 1930, Sect. III, 93.



Courtesy American Petroleum Institute.

Fig. 12.—Application of Thermodynamics to Chemical Reactions of Petroleum Products. (Francis and Kleinschmidt.)

(1) With the exception of methane and possibly ethane, all petroleum hydrocarbons are thermodynamically unstable at temperatures above about 200° C.

(2) No paraffin hydrocarbons can polymerize directly to higher hydrocarbons, and at cracking temperatures the paraffins are the least stable of all hydrocarbon types.

(3) The olefins are more resistant to heat than the paraffins and tend to polymerize below about 425° C. and to crack above that temperature. The iso-

merization of olefins to the corresponding cycloparaffins is a possible reaction at temperatures below about 425° C.

(4) The naphthenes are intermediate in their stability to heat between the paraffin and aromatic hydrocarbons. At higher temperatures the dehydrogenation of cyclohexanes to benzenoid hydrocarbons is favored, while the reverse change occurs in the presence of hydrogen at lower temperatures.

(5) The aromatic hydrocarbons, as a class, are most resistant to heat; particularly the large class of polynuclear aromatic materials, of which petroleum coke probably represents the limiting example.

The free energy calculations of Francis and Kleinschmidt lead to conclusions which are almost identical with those derived by Sachanen and Tilicheyev[7] from a calculation of the equilibrium constants of a large number of hydrocarbon reactions at 477° C. using the Nernst "approximation formula." Such thermodynamic considerations lead to the important conclusion, fully substantiated by experimental evidence, that most of the reactions occurring in practical cracking operations are of an irreversible character, in particular those involving the rupture of a C—C bond. Possible exceptions to this rule are the polymerization and depolymerization of monolefin hydrocarbons which exhibit a certain degree of reversibility. Depolymerization is complicated, however, by the occurrence of other reactions particularly at temperatures above 500° C. On the other hand, dehydrogenation and hydrogenation reactions of hydrocarbons are reversible under conditions within the somewhat narrow limits of stability of the hydrocarbons concerned.

ACTUAL STABILITY OF HYDROCARBONS[8]

Although the thermodynamic tendency for reactions to occur is determined by the free energy relationship existing under the conditions employed, experience has shown that in the cracking process the extent to which certain reactions proceed at the expense of other reactions is mainly dependent upon the *relative reaction velocities,* about which the laws of thermodynamics can tell us but little. In the range of temperature commonly used in commercial cracking operations of both liquid phase and vapor phase types, namely within the limits 400° to 650° C., experience indicates that the various series of hydrocarbons may be listed in the following order of decreasing tendency to crack (i.e., of increasing stability to thermal decomposition), the comparison being based on compounds of approximately the same molecular weights: (1) Paraffins; (2) monolefins; (3) diolefins; (4) naphthenes, mononuclear and polynuclear; (5) aromatics, mononuclear and polynuclear.[8a]

It should be emphasized that this purely qualitative classification of relative cracking tendencies is valid only within the temperature range 400° to 650° C., for at higher temperatures the diolefins become more stable than the naphthenes.

It has been further observed that the stability of the higher members of any given series increases with decreasing ratio of hydrogen to carbon in the molecule, i.e., the hydrocarbons most deficient in hydrogen are the most stable. An example of this rule is to be found in the polynuclear aromatic hydrocarbons. An exception to the rule is the higher naphthenes. In general, side chains in hydrocarbons have been found to be more stable to pyrolysis than the ends of straight chains.

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[7] *Ber.,* 1929, **62**, 658.

[8] Frolich (*Chem. Met. Eng.*, 1931, **38**, 343) gave a review and description of the mechanism of cracking.

[8a] *Cf.* Pease and Morton, *J.A.C.S.*, 1933, **55**, 3190.

Some investigators reverse the order of the paraffins and monolefins. For example, Tilicheyev and Feigin[9] concluded from their results on cracking various hydrocarbons prepared synthetically or separated from petroleum fractions at 425° C. that the ethylenic hydrocarbons are more rapidly decomposed than paraffin hydrocarbons. This difference became small with increasing molecular weight. Thompson[10] reported that saturated branched-chain hydrocarbons are less stable than saturated straight-chain hydrocarbons, and that olefinic hydrocarbons decompose more readily than saturated hydrocarbons. The stability of olefinic hydrocarbons is greater the nearer the double linkage is to the center of the chain. McKee and Szayna[11] have followed the cracking of several gasoline fractions (boiling points 120° to 126° C.), and also of a number of hydrocarbons (aromatics, olefins and paraffins) at temperatures of 405° to 420° C. by determining the critical temperatures of the materials at definite time intervals. Olefin hydrocarbons appear to be the most rapidly decomposed, saturated hydrocarbons less rapidly, and the gasoline fractions decomposed slowest. The aromatics (a mixture of toluene and benzene) were apparently unchanged even after being heated for several hours.

PRIMARY AND SECONDARY REACTIONS IN CRACKING

In spite of the fact that, thermodynamically speaking, all liquid hydrocarbons are inherently unstable at temperatures above about 200° C., noticeable decomposition usually does not occur until temperatures of 300° C. or over are attained.[12] Even at these temperatures the reaction velocity is very slow. As may well be imagined, the temperature of initial decomposition varies markedly with different individual hydrocarbons, and for a complex mixture of hydrocarbons, such as a petroleum fraction, it depends principally upon the nature of the more unstable hydrocarbons present in the mixture, and also possibly upon the pressure. The velocity of cracking of petroleum fractions is generally far too small for practical purposes at temperatures below 400° C.

The complexity of the cracking process is attributable not only to the heterogeneous character of the hydrocarbon mixtures employed but also to the fact that each individual hydrocarbon on pyrolysis undergoes a sequence of cracking reactions, the nature and extent of which depend upon a large number of factors. It is obviously extremely difficult to investigate the reactions occurring during the cracking of such complex mixtures of hydrocarbons. A much clearer insight into the mechanism of the reactions concerned can be gained from an experimental study of the pyrolysis of pure hydrocarbons and from the thermodynamic considerations previously discussed. By this means it is possible to differentiate between the initial or *primary reaction products* and the secondary changes which occur on more prolonged cracking. The primary products invariably undergo a further sequence of secondary changes which tend to obscure the course of the reactions, particularly under prolonged treatment at cracking temperatures.

As previously stated, the paraffin hydrocarbons undergo pyrolysis more readily than other types of hydrocarbons. The initial cracking reaction of the paraffin hydrocarbons is either (1) a dehydrogenation of the paraffin with the production of an olefin of the same number of carbon atoms or (2) a rupture of a C—C bond with the formation of a lower paraffin and an olefin. The first reaction, noticeable with the lower paraffins, becomes less and less important as molecular weight increases and would appear to be quite unimportant under practical cracking conditions. In the second (the principal) primary reaction, the point of fission of the C—C bond appears to follow the law of chance, but it has been stated that the influence of pressure is to force the point of cleavage towards the center of the paraffin molecule with the production of a lower paraffin and an olefin, both of about the same molecular weight. According to some observers the most stable paraffins are those with 12 to 15 carbon atoms, but this needs more experimental confirmation. After the primary cracking reactions have taken place, secondary changes intervene by which the lower paraffin is further decomposed through the fission of a C—C bond and the olefins produced also undergo decomposition.

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[9] *Repts. Conf. on Cracking Hydrogenation Grozny*, 1931, 1. 240; *Chem. Abs.*, 1932, 26, 1105.
[10] Abs. Theses Mass. Inst. Tech., 1931, 7, 51; *Brit. Chem. Abs.* A, 1931, 596.
[11] *Ind. Eng. Chem.*, 1930, 22, 953.
[12] Frolich, *loc. cit.*

The olefin hydrocarbons, which are rarely present in appreciable amounts in straight-run petroleum distillates and are to be regarded as the most important primary products of cracking, undergo decomposition in several ways. Polymerization reactions play an important rôle, particularly with olefins of higher molecular weights, and yield new compounds with molecular weights and boiling ranges higher than those of the original charging stock.[12a] Depolymerization can also occur with the formation of two olefins of lower molecular weight. And finally, simple cracking produces a diolefin and a paraffin hydrocarbon of lower molecular weight. The cyclicization of some of the monolefins to naphthenes is not improbable under cracking conditions.

The naphthene hydrocarbons may split and yield olefins at high temperatures (450° C. and above) and six-membered ring systems may be dehydrogenated to aromatic hydrocarbons. Naphthene hydrocarbons containing long side chains readily split off side chains at cracking temperatures.

The aromatic hydrocarbons, which are themselves formed from paraffin, olefin and naphthene hydrocarbons by a sequence of reactions at temperature of 550° C. and over, are very stable to heat, particularly the polynuclear members. They tend to form condensed ring systems in which the aromatic nuclei remain intact, hydrogen being simultaneously liberated. The aromatic hydrocarbons may be regarded as important coke-forming substances.[13]

Of the secondary changes taking place in the cracking of oils, polymerization of the olefins formed by the primary reactions is of very great importance. The high molecular weight material produced by such polymerization undergoes further cracking on prolonged exposure to high temperatures with the production of new unsaturated materials which can again undergo polymerization. The cumulative effect of this sequence of polymerizations and splitting reactions is the simultaneous formation of gaseous and low-boiling hydrocarbons, hydrogen, and more and more complex compounds of decreasing hydrogen content. Prolonged cracking invariably produces large amounts of petroleum coke which may be regarded as a highly polymerized hydrocarbon material of low hydrogen-carbon ratio. As previously pointed out, with decreasing hydrogen content the thermal stability and resistance to cracking increases markedly.

The above discussion refers to the cracking reactions predominating in the temperature range 400° to 600° C. At higher temperatures dehydrogenation reactions become very pronounced with greatly increased formation of aromatic hydrocarbons, much permanent gas, and coke.

[12a] The polymerized residues, after the removal of the lower-boiling constituents, may be employed, in conjunction with linseed oil, as a paint vehicle; Zilbermann, Jakubovitsch, Bolotin and Micheeva, *J. Chem. Ind. Russia*, 1933, No. 4, 16; *Chem. Abs.*, 1933, **27**, 5558.

[13] Sachanen and Tilicheyev, *Petroleum*, 1927, **23**, 521; *Brit. Chem. Abs.* **B**, 1927, 576; *Ber.*, 1929, **62**, 658; *Neft. Khoz.*, 1929, **16**, 223; *Chem. Abs.*, 1929, **23**, 4807. Singer, *Petroleum*, 1929, **25**, 893; *Brit. Chem. Abs.* **B**, 1930, 848.

PHYSICAL CHEMISTRY OF THE CRACKING PROCESS

A large number of workers have shown that the initial molecular breakdown of both pure saturated hydrocarbons and of petroleum fractions follows the law for homogeneous unimolecular reactions, and is therefore independent of the concentration.[14] Thus Geniesse and Reuter [15] studied the cracking of gas oil and of several naphthas at atmospheric pressure and showed that their results could be well expressed by the unimolecular equation

$$k = \frac{1}{t} \log_e \frac{a}{a - x}$$

where a = initial quantity of hydrocarbon; $a - x$ = quantity remaining at time t; k = reaction velocity coefficient.

This fits especially well at temperatures below 640° C. under conditions where the decomposition was not allowed to proceed too far. As the percentage decomposition increases the velocity constants decrease on account of the intervention of secondary reactions, such as polymerization, and the increasing thermal stability of the cracking stock through molecular rearrangement. Geniesse and Reuter found that the results of other workers on the pyrolysis of various pure hydrocarbons as well as their own observations of petroleum fractions can be represented by a family of curves of approximately equal slope (Fig. 13) indicating that the activation energies for the decomposition of all these hydrocarbons are about the same. In spite of the fact that Schneider and Frolich [16] have shown that reactions of the type

$$2C_3H_8 \longrightarrow C_2H_6 + C_4H_{10}$$
$$2C_3H_6 \longrightarrow C_2H_6 + C_4H_6$$

occur during the pyrolysis of a number of the simple paraffins and olefins, nevertheless these reactions, at first sight bimolecular, behave approximately as first order reactions.

Although all primary cracking reactions proper are thus approximately unimolecular, as soon as the secondary reactions become important (i.e., as the degree of decomposition is increased), the first order constant declines rather rapidly. This is to be ascribed partly to the occurrence of polymerization reactions since polymerization is a bimolecular process.[17] The velocity of polymerization reactions increases with rising temperature but much less rapidly than that of simple molecular decomposition.[18]

The heat effect of cracking is of considerable importance both from a practical and theoretical standpoint. The cracking process consists of a complex sequence of reactions, some of which are endothermic and some exothermic, so that the final heat effect depends on the character of the charging stock, the cracking temperature (which influences to some extent the type of cracking reactions predominating), and the degree of cracking. In general, purely cracking reactions such as the splitting of a C—C bond, and dehydrogenation reactions, such as the dehydrogenation of cyclohexane to benzene and of ethane to ethylene, are highly endothermic. On the other hand, polymerization reactions are usually exothermic. Frey and Hepp [19] have shown that during the pyrolysis of the lower paraffins to produce aromatic hydrocarbons the rapid initial highly endothermic reaction producing olefins (accompanied by a heat absorption of about 450 calories per gram) is followed by a slower aromatization reaction which is exothermic to the extent of about 190 calories per gram. Evidently, therefore, the conversion of olefins into aromatic hydrocarbons occurs as a series of changes, the overall heat effect of which is decidedly exothermic.

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[14] Kiss, *Ind. Eng. Chem.*, 1930, 22, 10.

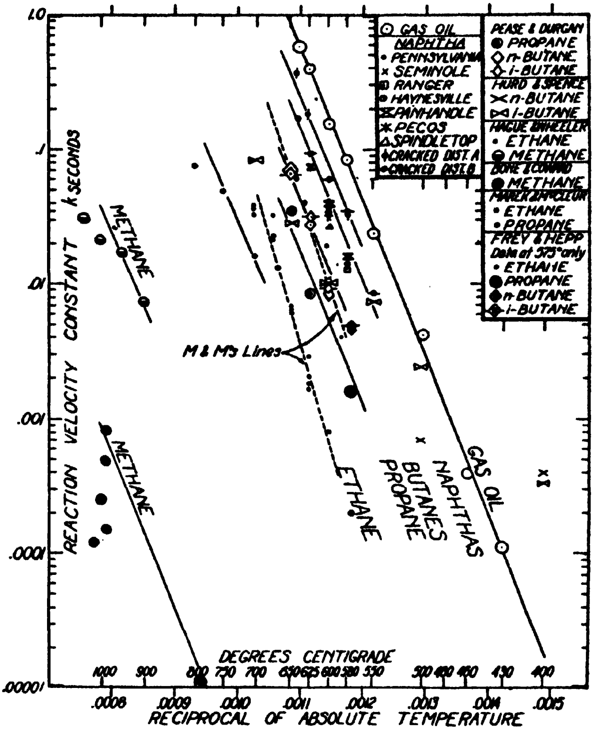
[15] *Ind. Eng. Chem.*, 1932, 24, 219.

[16] *Ind. Eng. Chem.*, 1931, 23, 1405.

[17] See for example, the work of Pease (*J.A.C.S.*, 1931, 53, 613) on the thermal polymerization of ethylene under pressure.

[18] At pressures higher than one atmosphere the polymerization of olefins is accelerated. This effect of pressure on cracking reactions is discussed later in this chapter.

[19] *Ind. Eng. Chem.*, 1932, 24, 282.



Courtesy Industrial and Engineering Chemistry.

FIG. 13.—Variations of Reaction Velocity Constant with Temperature. (Geniesse and Reuter.)

In practical cracking operations for the production of gasoline, however, endothermic reactions greatly predominate over exothermic reactions and the total heat effect is a negative one, being of the order of 500 calories per gram of gasoline formed.[20] For reasons already stated, the reader will rightly con-

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[20] Obryadchikov, *Repts. Conf. on Cracking Hydrogenation Grozny*, 1931, 1, 67; *Chem. Abs.*, 1932, 26, 1104.

The amount of heat absorbed during the cracking reaction per meter of tube (linear velocity of material through the tube being 1 meter per second) is expressed by the equation

$$Q \text{ reac.} = \frac{500 G_2 P_{400}\, 2^{\frac{t_{400}}{10}}}{100}$$

in which G_2 is the weight of the stock through the tube, P_{400} the percentage of cracked gasoline formed at 400° C., and t is the temperature of the liquid in this section of the tube (Obryadchikov, *Neft. Khoz.*, 1929, 16, 357; *Chem. Abs.*, 1929, 23, 4808).

In some instances, however, a figure of 250 calories per gram of 374° F. end point gasoline formed is used as the net total heat effect of cracking.

clude that the heat effect of cracking is a variable figure depending upon a number of factors.

FUNDAMENTAL FACTORS INFLUENCING CRACKING

Of the various factors influencing the extent and character of the thermal reactions of hydrocarbons the most important are temperature, duration of heating, pressure, character of heating surface or presence of catalytic materials, and the nature of the hydrocarbons undergoing pyrolysis.[20a] The following is a brief discussion of the effect of each of these factors, with special reference to commercial cracking operations.

Temperature. Temperature not only influences the type of cracking reactions which occur but also exerts a striking influence on the reaction velocity. Cracking of liquid petroleum hydrocarbons may begin at temperatures as low as 200° C., depending upon the character of the more unstable hydrocarbons present, but it is not sufficiently rapid for technical purposes until temperatures above 400° C. are attained. On the other hand Ryonosuke Abe[21] concluded, from the heating curves of petroleum oils taken at atmospheric pressure, that a temperature of 300° C. is necessary before cracking became fairly rapid. The velocity of cracking, although closely dependent upon the temperature, varies somewhat at any particular temperature for different types of oils.

As previously noted, the initial cracking reaction has been shown to be approximately unimolecular, and the velocity constant k can be represented by the equation

$$k = \frac{l}{t} \log_e \frac{a}{a - x}$$

Certain approximations become necessary in applying this formula to petroleum distillates, since the quantity of unchanged material cannot be readily determined. Geniesse and Reuter[22] have successfully applied it to the cracking of a Mid-Continent gas oil at atmospheric pressure by taking as unchanged material $(a - x)$ all the oil in the product after removal by distillation of the gas, gasoline, and higher-boiling products, i.e., all material boiling outside the range of the original fraction. The effect of temperature upon the velocity constants so obtained with the gas oil examined by Geniesse and Reuter could be represented by the formula

$$k = 28.8\, e^{-53{,}400/RT}$$

For this the activation energy is 53,400 calories per gram molecule. Data for a number of other pure hydrocarbons indicated that the activation energies of the cracking reaction are approximately the same except for hydrocarbons, such as ethylene, undergoing bimolecular polymerization reactions. Unfortunately for the above mode of computation, the unimolecular reaction constants tend to decline as the cracking proceeds because of secondary changes which are not of the first order.

It has repeatedly been stated[23] that the velocity of cracking is doubled for every 10° C. rise in temperature, but this is probably only a very rough approximation and the actual value appears to change somewhat less rapidly with the temperature of cracking. The experiments of Geniesse and Reuter indicated that the reaction rate of cracking a Mid-Continent gas oil at 1 atmosphere (and hence in the vapor phase) doubled for an increment of 14° C. at 450° C. and for an increment of 21° C. at 600° C. Leslie and Potthoff[24] reported that in the formation of gasoline from gas oil and heavy oil the yield doubled for every rise of 12° C.

[20a] The fundamental variables in mixed-phase cracking (time, temperature and pressure) and their effects on the yields and characteristics of the products are discussed by Sydnor, *Ind. Eng. Chem.*, 1934, **26**, 184.

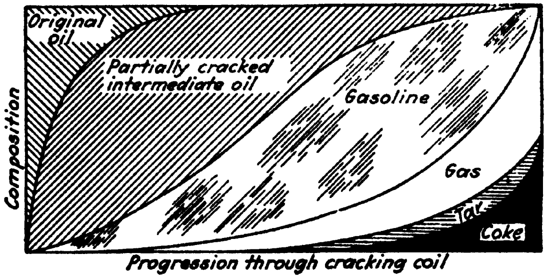
[21] *J.S.C.I.* (*Japan*), 1929, **32**, 152; *Chem. Abs.*, 1929, **23**, 5035. Waterman and te Nuyl (*Petroleum Z.*, 1931, **27**, 539; *Chem. Abs.*, 1931, **25**, 5976) report that with heavy distillates (vaseline oil) cracking was slight at 500° C. and became pronounced at temperatures of about 600° C.

[22] *Ind. Eng. Chem.*, 1932, **24**, 219.

[23] For example, Singer, *Petroleum Z.*, 1929, **25**, 893; 1930, **26**, 482. Humphreys, Rogers, and Paulus, U. S. Patent 1,553,861, Sept. 15, 1925; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1925, **19**, 3585.

At any one temperature the actual velocity of cracking depends definitely on the character of the charging stock. An investigation of this factor has been carried out by Sachanen and Tilicheyev[25] who studied the cracking of fractions of narrow boiling ranges, chiefly of Grozny oil, in a small shell still at final pressure of 61 to 100 atmospheres. At one particular temperature the rate of cracking was lowest for the lightest fractions and gradually increased for the heavier components. For example, under the same conditions of cracking a gasoline fraction (boiling 180° to 220° C., specific gravity 0.793) yielded 12 per cent of cracked gasoline (boiling up to 180° C., specific gravity 0.728) and an engine oil (boiling 250° to 280° C., specific gravity 0.910) gave 22.4 per cent of cracked gasoline (boiling up to 200° C., specific gravity 0.735).

In agreement with the conclusion that in the cracking process there is a progressive tendency for the production of hydrocarbons of increasing thermal stability, Sachanen and Tilicheyev found that cracked oils decompose at considerably slower rates than straight-run oils of comparable boiling range. Leslie and Potthoff observed that cracked residuum is decomposed at 427° C. at about half the velocity at which heavy fuel oil cracks. On the other hand, Geniesse and Reuter reported that pressure-cracked naphthas crack more easily than straight-run crude naphthas.


Original oil
Partially cracked intermediate oil
Gasoline
Gas
Tar
Coke
Composition
Progression through cracking coil

Courtesy Refiner and Natural Gasoline Manufacturer.

FIG. 14.—Degree of Cracking as a Function of Time of Contact. (Frolich.)

Duration of Cracking. As the time of contact of the hydrocarbons in the cracking zone is prolonged the primary cracking products undergo a series of secondary changes, the final result of which is to produce more and more fixed gas and coke. The formation of coke does not occur in the first stages of the cracking process and only begins when products of condensation (i.e., polymerized oils) in the form of high specific gravity oil have been produced. The velocity of coke formation increases with increasing time of cracking. The change of composition of the cracked products with increasing time of contact is shown graphically in a qualitative way in Figure 14.[26]

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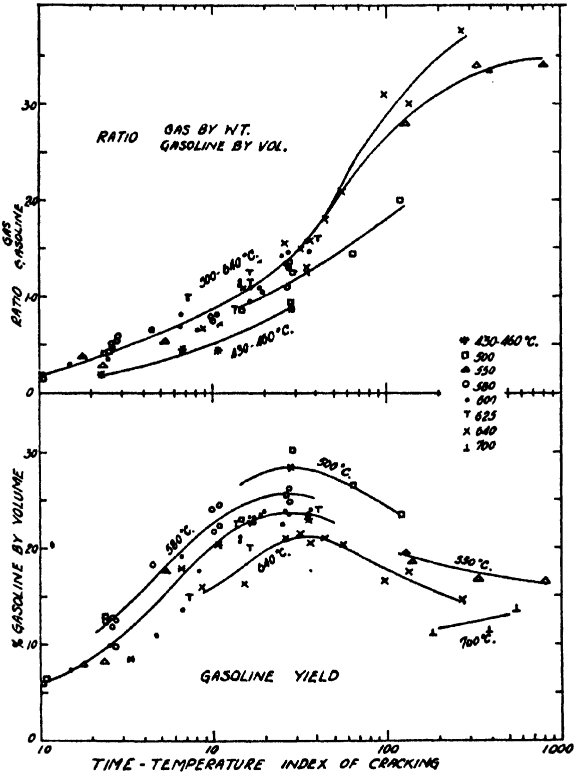
[24] *Ind. Eng. Chem.*, 1926, **18**, 776.

[25] *J. Inst. Pet. Tech.*, 1928, **14**, 761; *Petroleum*, 1927, **23**, 521.

[26] Strout, *Refiner*, 1929, **8**, 64; *Am. Pet. Inst. Proc. 10th Ann. Meeting*, 1930, 11 (1), Sect. III, 46; *Chem. Abs.*, 1930, **24**, 1965.

It has been shown by a large number of workers that prolongation of the cracking period has the same influence on the yield of products as an increase in the temperature of cracking, i.e., the results obtained at high temperatures and short times of contact can be duplicated approximately by using longer times of contact at lower temperatures. The validity of this rule, which is to be regarded as an approximation only, is restricted to the temperature range of commercial cracking reactions, i.e., 400° to 650° C. Geniesse and Reuter[27] found it convenient to consider the time and temperature factors together as a time-temperature index. Taking 480° C. as a standard temperature condition and assuming that the velocity of cracking is doubled for a rise of temperature of 17° C., this time-temperature index may be expressed as,



Courtesy Industrial and Engineering Chemistry.

FIG. 15.—Time-Temperature Index of Cracking of a Mid-Continent Gas Oil. (Geniesse and Reuter.)

$$\left(2^{\frac{T-480}{17}}\right) \times t$$

where T = cracking temperature in ° C.; and t = time of contact in minutes.

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[27] Ind. Eng. Chem., 1930, 22, 1274.

The influence of varying the time-temperature index on the yields of gasoline and on the ratio of gas to gasoline obtained in the cracking of a representative Mid-Continent gas oil at temperatures of 430° to 700° C. and at atmospheric pressure are shown in the appended series of curves (Fig. 15) by Geniesse and Reuter. In plotting these curves the logarithm of the time-temperature index was employed rather than its numerical value. From the curves it is seen that as this index increases the yield of gasoline increases rapidly until a maximum value is reached. From then on the yield decreases slowly as the index increases. The curves also indicate that for a given value of the time-temperature index the yield of gasoline is higher at the lower cracking temperatures. The ratio of gas to gasoline continuously increases with the time-temperature index, becoming very large for values of the index greater than that corresponding to the maximum yield of gasoline.

The parallel influence of time of contact and temperature on the degree of reaction is not restricted to the cracking of petroleum fractions for gasoline production but appears to be a general phenomenon in the pyrolysis of all hydrocarbons. For example, Frey and Hepp[28] showed that in the pyrolysis of gaseous paraffin hydrocarbons at high temperatures to yield aromatic liquids, variation in time or in temperature gave equivalent results with respect to the yield of volatile oils over a wide temperature range. It was found that the minimum values of contact time required to develop an approximate maximum yield of volatile oils at any particular temperature was related to that temperature by the empirical formula:

$$T = 691 - 100 \log t$$

where T = temperature; and t = time in minutes.

The influence of the time factor on the yields of gasoline from the cracking process is that gasoline production becomes slower and slower as cracking is prolonged and the total gasoline yield tends to approach a limit. Recycling experiments carried out by Sachanen and Tilicheyev, with a charging stock of light gas oil in a small shell still operating under pressure, showed that the gasoline yield was 17.5 per cent in the first pass, and increased to 55 per cent after four passes. After repeated runs the yield of gasoline seemed to approach a limit of about 60 per cent with moderate coke formation or 65 per cent with considerable coke production.[28a]

Pressure. In the temperature range (400° to 650° C.) normally used in liquid phase processes the more volatile hydrocarbons are above their critical temperatures and only the less volatile ones are in the liquid condition under pressure. With increasing pressures the more volatile hydrocarbons are dissolved to a greater degree in the liquefied heavy ends so that only at very high pressures is a true liquid phase (or homogeneous) system obtainable. Moreover, it is doubtful whether there is such a thing as a liquid phase process in the usual sense of the word. Operating conditions which would constitute a liquid phase for the charging stock will not continue to exist as the structure of the hydrocarbon molecules is broken down to form lower boiling fractions. With increasing conversion to lighter hydrocarbons (secured by increasing the time factor under constant temperature conditions) the ratio of vapor to liquid increases so that such processes obviously operate as a heterogeneous gas-liquid system. The influence of pressure on the character of the cracked products is closely dependent upon the degree to which solution of the cracked products in the liquefied oils takes place.

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[28] *Ind. Eng. Chem.*, 1932, **24**, 282.

[28a] This decrease in gasoline formation on recycling was also observed by Tarasov and Seledzhiev, *Neft. Khoz.*, 1932, **23**, 177; *Chem. Abs.*, 1933, **27**, 2022.

The great technical advantages of the use of higher pressures are that the best conditions for heat transfer, absence of local superheating and economy of fuel are thereby attained. The influence of pressure on the velocity of cracking has been the subject of a number of somewhat contradictory statements. It seems, however, that pressure exerts little influence on the velocity of cracking in the initial stages when the temperature and time of reaction are maintained constant. As cracking reactions proceed, however, the yield of gasoline undergoes a slight decrease probably because of polymerization of the unsaturated hydrocarbons into high-boiling compounds.[29] The apparent increase in the velocity of cracking with increased pressure is probably to be accounted for by the increased time of contact as a result of continued separation of material from the vapor phase to the liquid state and to the better heat transfer thus obtained.

From a theoretical standpoint there is no reason to suppose that increased pressure will favor the primary cracking reactions except by facilitating heat transfer. On the basis of Le Chatelier's theorem increased pressure should suppress the formation of uncondensible gaseous products. However, pressure undoubtedly plays a very important part in determining the course of the secondary changes in cracking operations. Since polymerization (of olefins) is a bimolecular reaction, the rate of which is proportional to the square of the pressure, it is to be expected that the use of high pressures will favor the polymerization of the unsaturated hydrocarbons initially formed in the first stages of the process, a phenomenon which has been repeatedly observed in the case of individual olefins. This is in accord with the observations made by numerous investigators that an increase in the pressure reduces the unsaturated hydrocarbon content of the resulting cracked gasoline.[30] Sachanen and Tilicheyev[31] found, for example, that when paraffin wax (melting point 53° C.) was cracked under 10 atmospheres pressure the gasoline produced had an iodine number of 107.8. When cracking was carried on under 40 atmospheres pressure the iodine number of the gasoline was 58.8. These figures indicate a decrease in the content of unsaturated hydrocarbons in the cracked gasoline by about one-half. Philippide[31a] noted when kerosene was cracked at 600° C. in an electrically heated tube that increasing the pressure from 1 to 20 atmospheres resulted in a decrease in the percentage of unsaturated hydrocarbons in the product.

This decrease in the proportion of unsaturated hydrocarbons at higher pressures is accompanied by the formation of polymerization products and of naphthenes. According to Frolich,[32] however, the favorable influence of pressure in promoting polymerization reactions is gradually counterbalanced by the increasing segregation of the olefins of high and medium molecular weight (which are the ones most readily polymerized) with rising pressure into the liquid phase where, by dilution with cracking stock, their rates of polymerization are slowed down considerably. The net result of this forcing by pressure of the vaporized olefins into the liquid phase is that polymerization and coke formation under certain conditions at first increase very rapidly with rising pressure, gradually increase more slowly, then pass through a maximum and at higher pressures coke formation actually declines.

In addition to its influence in depressing the content of unsaturated hydrocarbons in cracked benzines (already noted), increase of pressure also decreases the yields of gasoline obtained under a given combination of conditions particularly with intensive cracking when secondary changes become important. The use of increased pressures will tend to suppress gas formation in cracking, especially in dehydrogenation reactions in which the rate of dehydrogenation is retarded by raising the pressure.

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[29] Sachanen and Tilicheyev, *Oil and Gas J.*, 1929, **28**, 48. Kato (*J. Soc. Chem. Ind. Japan*, 1933, **36**, suppl. binding 226; *Chem. Abs.*, 1933, **27**, 3808) reports that both the cracking rate and yield of gasoline decrease with increase of pressure through the pressure range of 60 to 300 atmospheres.

[30] E.g., Singer, *Petroleum Z.*, 1929, **25**, 893; 1930, **26**, 482.

[31] *Ber.*, 1929, **62**, 658.

[31a] *Petroleum Z.*, 1932, **28** (51), 1; *Chem. Abs.*, 1933, **27**, 1493. See also Kato, *J. Soc. Chem. Ind. Japan*, 1932, **36**, suppl. binding 226; *Chem. Abs.*, 1933, **27**, 3808.

[32] *Chem. Met. Eng.*, 1931, **38**, 343.

In view of the fact that coke formation is mainly dependent upon polymerization and recracking reactions producing high boiling asphaltic residuum oils (which are to be regarded as the parent substances of coke), it is to be expected that pressure will exert some influence on coke formation. As previously noted, the development of coke, like polymerization reactions, increases with rising pressure, rapidly at first, and then more slowly until it ultimately passes through a maximum and then declines. This is explained on the basis of the slowing down of polymerization velocity as the higher olefins are forced by increasing pressure into solution in the liquid phase and consequently diluted. Frolich[33] stated that polymerization and recracking reactions, the precursors of coke formation, are greatly depressed at ordinary cracking temperatures under 600 to 1000 pounds pressure as compared with, say, 100 to 200 pounds pressure. On the other hand, Graetz[34] found that, contrary to general belief, the formation of coke appears to be independent of the pressure applied. In any case, the pressure factor is of less importance in coke formation than temperature, duration of heating, and character of the charging stock.

CATALYSTS IN CRACKING

The thermal reactions of hydrocarbons are greatly influenced by the presence of certain catalytic materials in the reaction zone. Catalysts tend to promote the rapid attainment of an equilibrium condition at any particular temperature but, where a large number of intermediate stages are possible as in the thermal reactions of hydrocarbons, selective catalysis may occur and one reaction may be accelerated by one particular contact material.

The fundamental equilibrium to which all systems of hydrocarbons tend to revert at temperatures above about 500° C. is the methane-hydrogen-carbon equilibrium represented by

$$C + 2H_2 \rightleftharpoons CH_4$$

The attainment of this equilibrium takes a considerable time even in the presence of active catalysts and in the absence of catalysts it is approached only at high temperatures.

An investigation of the catalytic effect of a number of substances on thermal decomposition of methane was made by Slater.[35] He concluded that the chemical nature of the catalyst, as well as the area of the surface exposed, is of great importance.

The researches of Schützenberger and Jonine,[36] Zelinsky,[37] Mayer and Altmayer,[38] Slater,[39] Cantelo,[40] Zanetti,[41] and a large number of other workers have shown that the elements of the VIIIth Group, iron, nickel, and cobalt, are very active catalysts in promoting the decomposition of hydrocarbons into carbon, hydrogen, and methane. It is possible that this reaction is affected by the intermediate formation of metallic carbides. On treating the products of carbonization taken from the wall of an iron tube used in the pyrolysis of petroleum at 650° C. with dilute mineral acid, Zelinsky obtained a gas of the composition methane 12 per cent, hydrogen 85 per cent, and unsaturated hydrocarbons (C_nH_{2n}) 2.2 per cent, and an analysis of the original material showed 30 per cent iron and 70 per cent carbon. Scheffer, Dokkum and Al[42] found evidence of the formation of an unstable nickel carbide at comparatively low temperatures during the decomposition of methane in the presence of that metal.

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[33] *Loc. cit.*

[34] *Chimie et Industrie,* 1930, **24**, 271.

[35] *J.C.S.*, 1916, **109**, 160.

[36] *Compt. rend.*, 1880, **91**, 823; *Chem. Soc. Abs.*, 1881, **40**, 705; *Ber.* 1880, **13**, 2428.

[37] *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1807. See Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, 1932, 349.

[38] See Mayer, Henseling, Altmayer, and Jacoby, *J. Gasbel.*, 1909, **52**, 166, 238, 305; *Chem. Abs.*, 1910, **4**, 2724.

[39] *J.C.S.*, 1916, **109**, 160.

[40] *J. Phys. Chem.*, 1924, **28**, 1036; 1926, **30**, 899, 1641.

[41] *Ind. Eng. Chem.*, 1916, **8**, 674.

Numerous statements have been made that the production of gasoline or of aromatic hydrocarbons may be promoted by the presence of various catalysts but none of these catalysts, with the exception of aluminum chloride and iron oxide, are used industrially to any extent. Thus Ostromislensky and Burshanadse[43] reported that by using a spiral of iron gauze in the pyrolysis of naphtha at 700° C. the yield of benzene obtained was increased from 7.75 per cent to 10.9 per cent, and that asbestos, pumice, iron oxide and carbon promoted the formation of hydrogen and carbon. Zelinsky proposed the use of zinc oxide for increasing the yield of aromatic hydrocarbons by high temperature cracking but doubt has been thrown on the utility of the substance by the work of Bjerregaard.[44] According to Snelling,[45] colloidal graphite considerably reduces the pressure necessary for the liquid phase cracking of naphtha to produce benzine. Later, Chamberlin and Bloom[46] observed that the carbon first formed exerts a catalytic effect on the formation of aromatic hydrocarbons in the pyrolysis of natural gas and similar results were reported by Fischer and Pichler[47] in the thermal polymerization of acetylene.

The use of activated aluminum as a catalyst with chlorinated petroleum hydrocarbons has been suggested.[48] The petroleum fraction is first chlorinated until a 65 per cent increase in weight occurs. The chlorinated petroleum, either alone or admixed with some of the original fraction, is then passed over activated aluminum at temperatures of 150 to 250° C. The aluminum is activated by treatment with the solution of a less electro-positive metal, which is thus deposited on the aluminum. This cracking process apparently involves the elimination of hydrogen chloride from the chlorinated petroleum, followed by thermal decomposition of the olefinic hydrocarbons thus formed.

A number of investigators agree that silica, porcelain, and siliceous materials are not active catalysts for the decomposition of the gaseous paraffins into their elements. Similarly copper and tungsten have little effect on the decomposition of hydrocarbons into carbon and hydrogen.[49] Copper tubes have been used by Chamberlin and Bloom[49] and by Wheeler and Wood[50] for the production of aromatic hydrocarbons by the high temperature pyrolysis of gaseous paraffin hydrocarbons. Iron and nickel, on the other hand, are active catalysts of the formation of carbon and hydrogen from methane. The carbon, resulting from the pyrolysis of natural gas, exhibits a selective activity in the conversion of paraffins to aromatics. With the lower molecular weight hydrocarbons decomposition seems to take place through intermediate formation of labile residues,[51] while, as previously mentioned, the higher molecular weight compounds split yielding one saturated and one unsaturated molecule as the primary reaction.

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[42] *Rec. trav. chim.*, 1926, **45**, 803.

[43] *J. Russ. Phys.-Chem. Soc.*, 1910, **42**, 195; *Petroleum Z.*, 1910, **5**, 1243; *Chem. Abs.*, 1911, **5**, 989.

[44] *Ind. Eng. Chem.*, 1915, **7**, 573.

[45] *Chem.-Ztg.*, 1915, **39**, 395; *Chem. Abs.*, 1915, **9**, 2148; British Patent 18,419, 1914; *J.S.C.I.*, 1915, **34**, 1045.

[46] *Ind. Eng. Chem.*, 1929, **21**, 945.

[47] *Brennstoff-Chem.*, 1929, **10**, 279.

[48] I. G. Farbenindustrie A.-G., British Patent 347,727, 1930.

[49] E.g., Stanley and Nash, *J.S.C.I.*, 1929, **48**, 1T; Chamberlin and Bloom, *Ind. Eng. Chem.*, 1929, **21**, 945.

[50] *Fuel*, 1928, **7**, 535; *Chem. Abs.*, 1929, **23**, 3212.

The action of aluminum chloride, which promotes the cracking of hydrocarbons even at low temperatures, is unique and warrants a chapter to itself (see Chapter 6).

With the exceptions of aluminum chloride and of iron, none of these substances is used for the production of gasoline by commercial cracking. Most cracking tubes are made of iron but their surfaces rapidly become covered with a deposit of carbonaceous materials which inhibits any catalytic activity the metal might exert. Among the catalytic cracking processes must also be classed those in which a mixture of oil and steam is subjected to decomposition in the presence of catalysts such as iron, nickel, or aluminum. In the Ramage process, for example, a mixture of hydrocarbon vapor and steam is led over a reducible metal oxide such as iron oxide.[52]

Although it has been repeatedly stated that certain specific catalysts are advantageous in promoting gasoline production and in simultaneously suppressing coke formation, the use of such catalysts in commercial cracking operations has been almost negligible.[53] It has been proposed, for example, to employ molten catalysts such as alkali metal cyanides, certain alloys, and other metallic catalysts.[53a] A large number of solid contact catalysts have been suggested as applicable in both the liquid and vapor phases, including difficultly reducible metallic oxides, certain metallic metaphosphates, activated carbonaceous materials, complex carbides such as iron-tungsten carbide, and elemental silicon. Volatile catalysts for vapor phase operation include mercury vapor and the halogens. Oil-soluble metallic acetylacetonates, particularly of the elements contained in Groups III to VII of the Periodic System, have been proposed as catalysts for liquid phase cracking.[54]

INFLUENCE OF THE CHARACTER OF THE CHARGING STOCK

The character of the charging stock is of much greater importance in influencing the yields of products of liquid phase cracking (i.e., under pressure below 500° C.) than in cracking at higher temperatures in the true vapor phase.

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[51] Bone and Coward, *J.C.S.*, 1908, **93**, 1197. For a discussion of the mechanism of the pyrolytic decomposition of paraffin hydrocarbons see also Chapters 2 and 4.

[52] U. S. Patent 1,687,890, Oct. 16, 1928; assigned to Gyro Process Corp. See also U. S. Patents 1,403,194, Jan. 10, 1922; 1,409,404, Mar. 14, 1922; 1,752,692, Apr. 1, 1930; and British Patents 338,904 and 338,905, 1929.

[53] For a review of a number of such patents, see Egloff, Lowry and Schaad, *J. Inst. Pet. Tech.*, 1930, **16**, 133-246.

[53a] Ivanyss (*Petroleum Z.*, 1933, **29** (20), 1; *Brit. Chem. Abs.* **B**, 1933, 612) employed iron, tin, aluminum and nickel together with some chlorides, e.g., calcium, magnesium zinc or ferric chloride. Aluminum chloride was found to be a better catalyst than any of the metals. Titanium, tantalum or tantalum alloys have also been suggested (Mittasch, Stern and Galle, U. S. Patent 1,922,491, Aug. 15, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 5181) as well as steel alloys containing 5 to 8 per cent of chromium and small amounts of aluminum, silicon, molybdenum, vanadium, titanium, beryllium or copper (Vereingte Stahlwerke A.-G., British Patents 382,355 and 384,016, 1932; *Chem. Abs.*, 1933, **27**, 4387). Ansolvo acids have been proposed also (Galle, Rosinsky and Hofmann, U. S. Patent 1,923,571, Aug. 22, 1933; *Chem. Abs.*, 1933, **27**, 5181). Ugarte (French Patent 665,604, 1928; *Chem. Abs.*, 1930, **24**, 954; Australian Patent 18,020, 1929; *Chem. Abs.*, 1930, **24**, 3897) cracked heavy hydrocarbons by mixing them with basic, acid or neutral nitrates and subjecting the mixture to a temperature not exceeding 390° C. Another method is passing the hydrocarbons through a bath of a molten metal in which silicon carbide is the catalyst (Seelig, German Patent 546,124, 1929; *Chem. Abs.*, 1932, **26**, 3369; German Patent 573,455, 1931; *Chem. Abs.*, 1933, **27**, 3068).

For descriptions of apparatus in which catalysts are employed, see Sinclair Refining Co., German Patent 475,836, 1925; *Chem. Abs.*, 1929, **23**, 3804; and German Patent 497,428, 1926; *Chem. Abs.*, 1930, **24**, 3637; Seigle, U. S. Patent 1,913,061, June 6, 1933; *Chem. Abs.*, 1933, **27**, 4378; I. G. Farbenindustrie A.-G., French Patent 681,404, 1929; *Chem. Abs.*, 1930, **24**, 4385.

[54] I. G. Farbenindustrie A.-G., British Patent 337,046, 1929; *Brit. Chem. Abs.* **B**, 1931, 54.

In the latter, variations in the character of the charging stock exert but little influence on the yield and nature of the products, particularly gas, gasoline, and tar, under comparable conditions.[55]

In a discussion of the influence of the charging stock on cracking operations it is necessary to repeat many of the items previously mentioned. Such a repetition, however, will serve as a brief summary of the fundamental features of cracking.

In low-temperature cracking the character of the charging stock greatly influences, first, the velocity of cracking. On the basis of hydrocarbons of approximately equal molecular weights, the relative ease of cracking of the various series is in the order: paraffins, naphthenes, and aromatics (most difficult). Again, at a given temperature the higher boiling petroleum fractions crack more rapidly than do the lower fractions, and cracked products undergo re-cracking much more slowly than the original materials. Second, other factors being the same, it may be expected that the type of charging stock will influence the chemical composition of the gasoline produced. For example, a highly naphthenic distillate might be expected to yield a gasoline containing an abnormally large proportion of naphthenic and aromatic hydrocarbons. The constitution of the gasoline depends also to a large degree upon other factors, the most important of which are the temperature and duration of heating. Third, experience has shown that the yield of gasoline from different charging stocks (high-boiling petroleum distillates and heavy crude oils) varies somewhat with oils from different sources. Fourth, the rate of coke-formation, according to Singer,[56] depends upon the chemical composition of the charging stock, paraffinic stocks producing less coke than paraffin-free or asphaltic oils under similar conditions of cracking. He stated that kerosene yields practically no coke, solar and spindle oils, very little, and machine and cylinder oils, large quantities, while tars greatly increase the formation of coke. The yield of coke appears to be of greater importance in determining the details of a cracking operation than are the yields of cracked gasoline (which are the same for a given temperature and cracking time from heavy crude oils and mazout).[57]

As already noted, oils containing a relatively large proportion of higher aromatic hydrocarbons tend to form larger quantities of coke.

COMMERCIAL CRACKING PROCESSES

As has been mentioned previously, it is neither necessary nor desirable to enter into a detailed description of the various types of cracking plants now employed for the production of motor fuels from higher-boiling petroleum fractions or from topped or reduced crudes. The technical literature on the subject is voluminous and the number of processes is great and increasing rapidly.[58] To the petroleum chemist interested in the manufacture of organic chemicals, the principal interest in cracking is associated with the by-products of the process, and particularly with the gaseous by-products, which are valuable sources of large quantities of the lower olefins. In the following brief description of commercial cracking special attention is given to modern tendencies in vapor and liquid phase cracking operations.

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[55] E.g., Rittman, *Ind. Eng. Chem.*, 1915, 7, 945; Osterstrom and Wagner, *Proc. Amer. Pet. Inst.*, 1930, 11, 1.

[56] *Petroleum Z.*, 1929, **25**, 893; 1930, **26**, 482; *Brit. Chem. Abs.* **B**, 1930, 848.

[57] Mazout is the residual fuel oil from Russian petroleum.

[58] For a detailed description of commercial processes, see Leslie, "Motor Fuels," The Chemical Catalog Co., Inc., New York, 1923; Brownlee, *Chem. Met. Eng.*, 1924, **31**, 737, 812, 848; Ellis and Meigs, "Gasoline and Other Motor Fuels," D. Van Nostrand Co., New York, 1925; Dunstan and Pitkethly, *Trans. Fuel Conference, World Power Conference, London, 1928*, 1929, 1, 693; Sachanen, and Tilicheyev, "The Chemistry and Technology of Cracking," The Chemical Catalog Co., Inc., New York, 1932; Egloff and Nelson, *Nat. Pet. News*, 1930, **22** (3), 30.

Liquid Phase Processes. One of the first important developments in liquid phase cracking for gasoline production was that of Burton, subsequently improved by Clark. In this process gasoline was formed by a simple pressure distillation (under about 5 atmospheres pressure) in a steel shell supplied with tubes as heating surfaces. Thus, on heating 200 barrels of gas oil, or similar distillate, in a Burton still of 250 barrels capacity, under a pressure of 75 to 80 pounds per square inch, cracking began at about 340° C. Slow distillation for a period of 40 to 45 hours with a gradual rise in temperature to about 430° C. yielded a pressure distillate equivalent to about 60 to 65 per cent of the volume of the charging stock and about one-half of this pressure distillate was obtained as gasoline of 440° F. end point ("unsaturation" to sulphuric acid, about 10 to 12 per cent). The overall yield of gasoline was therefore of the order of 30 per cent. The method of pressure distillation employed in the Burton process possessed the disadvantages of very low capacity and undue coke-formation through local overheating. For this reason, the pressure distillation method has been almost entirely superseded by the continuous tube furnace which has the advantages of high capacity, reduced coke-formation, increased fuel efficiency, and, most important, ability to operate under very high pressures. Two well-known liquid-phase processes are those of Dubbs, using pressures of 150 to 400 pounds per square inch, and of Cross, operating at much higher pressures, 800 to 1000 pounds per square inch. Other liquid phase processes are associated with the names, Holmes-Manley, Fleming, Jenkins, and Ellis.

In modern liquid phase operation, as exemplified by the processes of Dubbs and Cross, the charging stock is preheated in a series of tubes ("cracking coils") through which the oil passes at a high velocity. The period of contact of the oil in the cracking coils is maintained sufficiently low to prevent any substantial decomposition of the oil at this stage.[59] The oil thus preheated to the temperature of incipient cracking is passed into a larger chamber (called the "soaker") where its velocity is arrested and cracking is allowed to continue to the desired point. Thus, while the initial heating of the oil takes place in the tubes in which little or no coke is deposited, the actual cracking occurs in the soaking drums, which are so designed as to hold a considerable amount of coke before cleaning out is necessary. In the Cross process the average time of reaction in the soaking drum is about 20 minutes, but this may vary according to the mode of operation. On leaving the soaking drum the products of reaction pass to a low pressure separator, where tar residue separates, and thence to a bubble tower which yields an overhead distillate of gasoline and a higher boiling residue (intermediate in boiling range between the distillate and the separated tarry residue), the latter being recycled.

In the "tube and tank" process developed by Ellis, the oil is first heated to a temperature of about 450° to 540° C. (850° to 1000° F.) by being passed through about one hundred small (4 to 4½ inch) tubes set in a furnace. From these tubes, the oil is discharged into an insulated reaction chamber built outside the furnace. A pressure of 250 to 1000 pounds is maintained on the reaction chamber. The more volatile products of the reaction leave the chamber through a pressure relief valve located at the end of the chamber opposite to that at which the oil enters. After leaving the reaction chamber the volatile products pass through a tar-separator, and thus to a bubble tower in which the lighter and heavier components are separated.

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[59] This condition is general with respect to the later types of cracking processes. In many of the older types a portion of the cracking coil also served as a soaking zone.

The products of liquid phase cracking consist of gas, gasoline, residual oil and coke. The yields of gasoline depend very largely upon the degree of cracking (or the extent of recycling), the nature of the charging stock, and the operating conditions. In general, larger quantities of gasoline are obtainable from lower-boiling petroleum distillates such as kerosene and gas oil, than from heavy oils such as fuel oils. By excessive cracking, yields of cracked gasoline as high as 70 per cent, based on the charging stock, have been obtained but only at the expense of forming much gas and coke together with a low quality residuum oil. Milder cracking conditions with production of less gas and coke and a higher quality residual oil yield from about 30 per cent to 55 per cent of gasoline, depending upon the character of charging stock. The residual oil from cracking operations can be further separated by distillation into such products as furnace oil, fuel oil, and Diesel oil.

According to Singer[60] the liquid phase cracking of Grozny and Surakhani mazouts and heavy crudes is carried out in Russia in two ways, namely (1) under mild conditions producing principally gasoline and fuel oil, and (2) by prolonged cracking to yield gasoline, coke and gas. The first method gives about 1 per cent of coke and 35 per cent of cracked gasoline, the coke formation being constant for equal gasoline yields, and the second, 57 per cent of motor spirits and 15 per cent of coke.

The formation of coke or carbon during cracking processes is said to be largely eliminated by cracking with superheated steam[61] at 1500 pounds pressure at 425° C. (815° F.). This same effect is secured by cracking liquid hydrocarbons (at 426° to 565° C. and 1000 to 5000 pounds pressure) in the presence of hydrogen, the proportion of the latter and the rate at which the reaction products are cooled precluding appreciable hydrogenation.[61a]

The gasoline obtained by liquid phase processes, i.e., cracking under pressure, differs in important respects from that produced by vapor phase, high temperature cracking. Liquid phase cracked gasoline possesses a lower unsaturated hydrocarbon content and much less tendency to gumming (on account of its lower content of diolefinic and similar reactive hydrocarbon types) than the vapor phase product. On the other hand, its anti-knock value is usually distinctly less than that of vapor phase gasoline and this fact is already exerting considerable influence on the cracking art. The increasing demand for motor fuels of high octane number (far higher, possibly, than is often necessary for most commercial motor engines) is a factor calculated to favor the development of high temperature cracking. However, at the present time liquid phase processes produce the major portion of the world's cracked gasoline supply and vapor phase operation is only in its preliminary stage of development. In order to improve the anti-knock quality of the cracked motor fuel, there is a tendency in liquid phase processes towards operation at higher temperatures.

VAPOR PHASE CRACKING

Vapor phase processes, operating at temperatures in the range 500° to 600° C. at atmospheric or only slightly superatmospheric pressure, possess the disadvantages of high fuel consumption, large production of gases and coke, and heavy up-keep and operating costs. On the other hand, they yield gasolines of high anti-knock value, and on this account, vapor phase operation is likely to undergo considerable expansion and development. The large production of gases rich in reactive unsaturated hydrocarbons by vapor phase processes, though a disadvantage to the refiner, is of profound interest to the chemist.[61b]

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[60] *Petroleum,* 1929, 25, 893; 1930, 26, 482; *Brit. Chem. Abs.* **B**, 1930, 848.

[61] Hancock and Boyle, U. S. Patent 1,576,742, March 16, 1926.

[61a] Ayres, British Patent 388,225, 1932; assigned to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1933, 340.

Of the older vapor phase processes those of Greenstreet, Rittmann, Hall and Parker were operated under pressures of 60 to 150 pounds per square inch at temperatures above 550° C., while the Alexander and Ramage processes were worked at atmospheric or only slightly superatmospheric pressure.[62]

The Ramage process[63] has been considerably improved and, under the name of the Gyro process, bids fair to attain a measure of popularity. The vapor of the hydrocarbons to be cracked, admixed with steam, is passed over a reducible metallic oxide, in particular ferrous oxide, at temperatures of 550° to 600° C. The proportions of steam and hydrocarbon vapor are such as to avoid oxidation of ferrous oxide to ferric oxide as far as possible, and its reduction to metallic iron. The following reactions are used by Ramage to illustrate the process:

$$\text{(1)}\quad C_nH_{2n+2} + Fe_2O_3 \longrightarrow C_nH_{2n} + 2FeO + H_2O$$

$$\text{(2)}\quad C_{16}H_{32} + 2C_8H_{16} \longrightarrow 4C_4H_8 + 8C_2H_4$$

$$\text{(3)}\quad C_2H_4 + 2Fe_2O_3 \longrightarrow 2C + 4FeO + 2H_2O$$

$$\text{(4)}\quad C + Fe_2O_3 \longrightarrow 2FeO + CO\ \ (550^\circ\ C.)$$

$$\text{(5)}\quad H_2O + 2FeO \longrightarrow Fe_2O_3 + H_2\ \ (500^\circ \text{ to } 600^\circ\ C.)$$

The hydrogen evolved according to reaction 5 is assumed to combine with the unsaturated hydrocarbons formed in reactions 1 and 2. On a commercial scale a positive pressure of a few pounds per square inch was employed and it was necessary to blow the iron oxide with air for a few minutes at the end of every 24-hours working operation. In a later development of this process described by Ramage,[64] heavy oils are passed with 1 to 2 per cent of steam over ferric oxide at 420° to 540° C., the resulting (largely olefinic) vapors with 10 to 20 per cent of steam are again passed over finely divided iron at 620° C. and with a further 20 to 40 per cent of steam the operation is repeated at 700° C. or over. An aromatic motor fuel together with gaseous products (e.g., hydrogen, carbon monoxide, methane and ethane) is obtained.

Recent developments of the older Ramage process in the form of the Gyro process have been described by Wagner.[65] In this process the oil is vaporized, mixed with superheated steam in quantity not exceeding 3 per cent by weight of the vapors and the mixture raised almost instantaneously to the cracking temperature of about 535° C. Reaction is allowed to take place in a converter of parallel tubes which in the past have sometimes been fitted with a catalytic core. The conversion is said to be complete in 2 seconds and the pressure on the system is about 15 to 25 pounds per square inch.[66] Wagner[67] stated that by careful temperature control the formation of carbon or coke and excessive amounts of gas can be minimized. A variation of 5° F. in the reaction temperature, other conditions being constant, is said to cause wide fluctuation in the proportion between fixed gas and motor spirit. Changes in the character of the charging stock exert less influence than the factors of heat transfer and flow and temperature control, and have much less effect than in liquid phase cracking. The yields of products obtained from the Gyro process vary, as might be expected, but the fixed gas yields are always high (at least twice as great as that obtained in ordinary liquid phase operation). By cracking gas oil yields of motor fuel of about 60 per cent and of dry gas of 30 per cent were obtained. The gas produced may be partly converted by pyrolysis into a gasoline of high anti-knock value so that the gasoline yield may be increased to about 75 per cent by this subsequent treatment of the gas. Wagner has given some results obtained in a small plant operating with a wide variety of charging stocks. Distillates ranging from 46.5° to 54.8° A.P.I. gravity with end points within the U. S. motor gasoline limit were obtained in yields of 43 to 64 per cent. The gasoline, obtained from the Gyro process contains 40 to 45 per cent of unsaturated hydrocarbons and about an equal proportion of aromatics, the balance being naphthenes with possibly traces of paraffins.

[61b] Wagner (*Ind. Eng. Chem.*, 1934, **26**, 188) discussed two types of vapor-phase cracking operations: (1) at high pressure at 950° to 1050° F. (exemplified by the de Florez process) and (2) at higher temperatures and low pressure (Gyro process).

[62] The various stages in the development of vapor-phase processes have been described by Auld, *Petroleum Times*, 1929, 21, 99, 158.

[63] U. S. Patents 1,403,194, Jan. 1, 1922; and 1,409,404, Mar. 14, 1922.

[64] U. S. Patent 1,752,692, Jan. 4, 1930; British Patent 338,904, 1929. See also British Patent 338,905, 1929.

[65] *Oil and Gas J.*, 1929, **27** (49), 46; *Chem. Abs.*, 1929, **23**, 4052; *Nat. Petroleum News*, 1929, April 24, 40; *J. Inst. Pet. Tech.*, 1929, **15**, 484; *Chem. Abs.*, 1929, **23**, 5564; *Refiner*, 1929, **8** (11), 80; *Chem. Abs.*, 1930, **24**, 2281; Ramage, U. S. Patent 1,900,997, Mar. 14, 1933; *Chem. Abs.*, 1933, **27**, 3064.

[66] Osterstrom and Wagner, British Patent 317,507, 1929; Australian Patent 13,623, 1928; French Patent 654,282, 1928.

[67] *J. Inst. Pet. Tech.*, 1929, **15**, 484; *Nat. Pet. News*, 1929, **29** (17), 40-a.

The deFlorez [68] process, which operates in the vapor phase at temperatures of 565° to 590° C. (1050° to 1100° F.) under a pressure of 80 pounds per square inch, is of interest. Although it is known that the use of increased pressure results in the formation of gasoline of lower unsaturation and diminishing gum-forming properties, deFlorez found that the effect becomes well marked even at pressures of the order of 50 to 60 pounds per square inch and at the temperatures indicated above. Furthermore the anti-knock quality of the gasoline is not appreciably depressed as a result of the reduced unsaturated content. The yields in Table 25 are reported by deFlorez for three typical oils cracked at 1050° to 1100° F. and 80 pounds pressure.

TABLE 25.—*Yields of Three Typical Oils Cracked at 1050° to 1100° F. and 80 Pounds Pressure.*

		Oil	
Yields (per cent)	Pa. Gas Oil	Calif. Gas Oil	Venezuela Crude
Gasoline distillate	61.4	53.9	36.4
Residuum	7.9	18.7	56.0
Gas	29.2	27.0	6.1

Gasoline obtained by this process is said to possess excellent anti-knock qualities.

The deFlorez furnace has been successfully used for "reforming" straight-run paraffinic gasoline to increase its anti-knock property, using a temperature of 925° F. and pressures as high as 1000 pounds per square inch. The recovery of cracked gasoline was as high as 86 to 88 per cent.[69]

A vapor phase cracking process developed by Stockman [70] uses steam or an inert gas to vaporize the oil feed. The oil vapors pass to a reaction chamber where they are cracked by heat from gases heated in a battery of stoves.[71] According to Sachs [72] the principles upon which such a vapor phase process is based are: the complete vaporization of the oil prior to passing to the cracking zone, heating the dry vapors by commingling them with hot inert gases and exposure of this hot mixture of gases to ceramic materials only. The reaction chamber is designed to allow time for optimum conversion per single passage at about 638° C. (1000° F.) and pressure is necessary only to overcome friction to ensure good circulation or to limit gaseous volume. In this process the yields of high anti-knock quality motor fuel vary according to the nature of the charging stock. With gas oil as charging stock, yields of cracked gasoline up to 80 per cent are said to be obtained.[73]

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[68] DeFlorez, *Nat. Pet. News*, 1929, **29** (17), 75; *ibid.*, 1929, **29** (49), 33; *Oil and Gas J.*, 1929, **27** (50), 154; *Proc. Amer. Pet. Inst.*, 1930, **9**, 111; see also Truesdell, *Nat. Pet. News*, 1929, **29** (18), 69.

[69] Brooks, *J. Inst. Pet. Tech.*, 1932, **18**, 260.

[70] *Oil and Gas J.*, 1929, July 11, 138.

[71] Balmer, British Patent 317,508, 1928; assigned to Petroleum Conversion Corporation; *Chem. Abs.*, 1930, **24**, 2283.

[72] *Refiner*, 1930, **9**, (1), 70.

Silicates either alone or impregnated with about 1 per cent of nickel or cobalt,[73a] or chromium or nickel alloys containing small proportions of silicon, zinc, iron, aluminum, molybdenum or titanium [73b] have been suggested as catalysts for the cracking of petroleum oils in the presence of steam.

Other vapor phase processes are those developed by Pratt [74] and by Leamon.[75]

On account of their high content of unsaturated hydrocarbons, particularly those of the diolefinic type, cracked gasolines from high temperature vapor phase operations are difficult to refine and have strong tendencies to gumming. Vapor phase refining with fuller's earth at 600° to 650° F. and 1000 pounds per square inch pressure has been used in the treatment of gasolines from the Gyro process.[75a]

Gaseous Products of Cracking

While practically all cracking processes form quantities of permanent gas (or cracking gas), the yield and composition of the gas so produced depends upon a number of factors, such as the type of plant and its operating conditions, but more particularly upon the temperature and duration of heating. The nature of the charging stock does not appear to influence greatly either the yield or the composition of the permanent gas. Particularly is this true in high temperature, or vapor phase, cracking where the gases produced by cracking such widely different charging stocks as Pennsylvania gas oil and crude shale oil have been found to have similar compositions.

Vapor phase cracking normally yields over 1000 cubic feet of gas per barrel of oil cracked. In contrast, the gas yield from liquid phase cracking varies from 100 to 450 cubic feet per barrel. Normal vapor phase cracking produces roughly the same weight of gas as of motor fuel, but if the temperature of cracking is raised to 700°, or higher, the yield of gas is greatly increased. High temperature cracking, especially of comparatively low grade hydrocarbon materials, for the production of large quantities of gas rich in olefin hydrocarbons, might easily be of economic significance.

The quantities of gas available from cracking operations are very large, and Egloff has estimated that the volume of gas produced by cracking processes in 1927 was of the order of 200,000,000,000 cubic feet. Wagner [76] stated that in a Gyro plant a throughput of 4000 barrels of gas oil produced 5,000,000 cubic feet of gas containing olefin gases to the extent of 1,350,000 cubic feet of ethylene, 800,000 cubic feet of propylene, and 450,000 cubic feet of butylenes. As the cracking process is extended to meet the demands for motor fuel the available supply of these valuable olefin gases will be further increased. Moreover, it appears probable that the cracking process will be ultimately applied to such substances as low temperature coal tar, shale oil, and other low grade hydrocarbon materials.

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[73] *Oil and Gas J.*, 1929, Sept. 19, 46.

[73a] Houdry, British Patent 388,189, 1933; assigned to Houdry Process Corp.; *Chem. Abs.*, 1933, 27, 4664.

[73b] Goldsbrough, British Patent 371,042, 1930; *Chem. Abs.*, 1933, 27, 2563.

[74] Krase, *Chem. Met. Eng.*, 1930, 37, 624. Pratt, U. S. Patent 1,752,264, March 25, 1930; British Patent 293,829, 1928.

[75] Staley, *Petr. Eng.*, 1931, (1), 3, 40.

[75a] Holland, *Refiner*, 1932, 11, 26.

[76] *J. Inst. Pet. Tech.*, 1929, 15, 484.

It is obvious that vapor phase high temperature cracking processes supply a gas valuable from the point of view of the synthesis of chemical products, since gaseous olefins are its principal constituent. As previously noted, the production of large quantities of gaseous olefins by vapor phase cracking is a fact of prime importance to the chemical industry, since these olefins can be converted into a variety of chemical substances of great industrial value.

COMPOSITION OF CRACKING GAS

The composition of cracking gas depends chiefly upon the temperature of cracking. Liquid phase cracking at temperatures of 450° to 480° C. yields a gas containing large proportions of gaseous paraffin hydrocarbons, comparatively small amounts of gaseous olefins, and only a little hydrogen. Propylene appears to be its principal olefinic constituent, ethylene occurring to a less extent, and practically no diolefins are present. On the other hand, vapor phase cracking gas is relatively rich in olefins (up to 60 per cent of the total), ethylene being the predominating constituent. Moreover, diolefins, chiefly butadiene, are present to the extent of 2 per cent, as well as paraffin hydrocarbons, chiefly methane and ethane, and hydrogen (up to 10 per cent).

Brooks and his co-workers[77] have recorded some analyses of gases taken at intervals during the pressure distillation of Jennings (La.) reduced oil boiling above 265° C., and of paraffin. (See Table 26.) The temperature of the still was, of course, rising throughout.

TABLE 26.—*Analysis of Gases Evolved During Pressure Distillation of Jennings Crude and of Paraffin, under 100 Pounds Pressure.*

	Jennings Reduced Crude			Paraffins		
	I	II	III	I	II	III
Temp. of still ° C.	340	415	422	417	432	437
CO_2	1.2	0.5	0.0	0.0	0.0	0.0
CO	1.2	0.5	1.3	0.0	0.0	0.0
C_nH_{2n}	15.4	15.3	13.0	25.4	37.0	33.5
H_2	0.0	4.0	4.4	0.3	0.9	3.0
C_nH_{2n+2}	81.5	79.7	81.3	74.3	62.1	63.5

Egloff[78] recorded the analyses of some gases obtained from liquid phase cracking (Dubbs process). The majority of these analyses indicate a rather high proportion of paraffin hydrocarbons (about 73 to 88 per cent). Ethylene, propylene and butylene appear to be the principal olefins in such gases and some hydrogen is also present.

A typical analysis of a vapor phase cracking gas from the Gyro process made by Wagner[79] is given in Table 27.

TABLE 27.—*Analysis of a Vapor Phase Cracking Gas from the Gyro Process.*

Constituent	Per Cent	Constituent	Per Cent
$CO_2 + H_2S$	0.25	Propylene	16.00
CO	0.15	Butylenes	9.00
H_2	7.00	Butadiene	1.00
Ethylene	27.00	Saturated hydrocarbons	39.00

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[77] Brooks, Bacon, Padgett, and Humphrey, *Ind. Eng. Chem.*, 1915, 7, 180.

[78] See Rogers, "Manual of Industrial Chemistry," 5th Edition, D. Van Nostrand Co., New York, 1931, 878.

[79] *Loc. cit.* These results obtained with a Pennsylvania gas oil. The hydrogen sulphide content of the gas will vary with the sulphur content of the charging stock.

Wagner, in a later contribution,[80] gave the analyses of typical gases from the vapor phase (Gyro) and liquid phase (Cross) processes as shown in Table 28.

TABLE 28.—*Analyses of Gases from the Gyro and Cross Processes.*

	Cross Process	Gyro Process
	Per Cent	
Methane + hydrogen	46.3	35.4
Ethylene	1.2	22.9
Ethane	16.6	13.3
Propylene	5.3	18.1
Propane	16.2	0.0
Butenes and butadiene	4.3	5.5
Butanes	6.1	1.4
C_5 and heavier	3.7	3.4

There thus appears to be little or no propane in the gases from the Gyro process, but there is some doubt as to the accuracy of this determination. It is believed possible that there may be cycloparaffins (cyclobutane) present, a point not settled definitely. Isobutene and butadiene are also present as well as 1-butene and 2-butene, but the quantitative relationships existing between these compounds are not yet known. Wagner further stated that, contrary to previous reports on the subject, it is now known that some effect upon gas composition is caused by changing the charging stock.

Dunstan[81] quoted the following figures for the unsaturated hydrocarbon content (amounting to 55 per cent of the total gas) in a vapor phase cracking gas:

Constituent	Per Cent	Constituent	Per Cent
Ethylene	54.0	Amylenes	1.7
Propylene	28.0	Higher olefins	6.1
Butylenes	9.0	Butadiene	1.2

Markovich and Pigulevski[81a] divided the gases from the vapor phase cracking at 580° to 620° C. of a Russian crude oil into 3 fractions, viz.: (I) a light fraction consisting of fixed gases and representing 20 per cent by weight of the total gaseous material; (II) a wet gas condensate representing 76.5 per cent of the total; and (III) gases remaining dissolved in the gasoline fraction and representing about 3.5 per cent of the total. The compositions by weight of these three fractions are given in Table 29.

Romoli-Venturi[82] reported that by compressing the gases formed during the cracking of petroleum residues (mazout, fuel oil, and other fractions) liquid hydrocarbons, amounting to 5 to 10 per cent of the original material, are obtained. These hydrocarbons, as indicated by the analysis of their bromine and hypochlorous acid reaction products, consist almost entirely of hydrocarbons of the diolefin and diacetylene series.

Thus vapor phase cracking gas is invariably a complex mixture containing paraffins, olefins, diolefins, hydrogen, and probably a little acetylene as well as sulphuretted hydrogen and carbon monoxide. It has been stated that of the butylenes present in vapor phase cracking gas, isobutylene predominates over its isomers.

[80] *Refiner,* 1930, 10 (6), 70.
[81] *J. Roy. Soc. Arts,* 1928, 76, 922, 945, 985, 1001; *Chem. Abs.,* 1928, 22, 4235, 4781.
[81a] *Refiner,* 1932, 11, 348; *Chem. Abs.,* 1932, 26, 4456.
[82] *Ann. chim. appl.,* 1930, 20, 18; *Brit. Chem. Abs.* B, 1930, 357; *Chem. Abs.,* 1930, 24, 2870.

TABLE 29.—*Composition of Components of Vapor Phase Cracking Gas.*

Per Cent by Weight

Component	I Fixed Gas	II Wet Gas	III Gases Dissolved in Gasoline
H_2	2.4	0.2	—
O_2, CO_2, N_2	3.5	0.4	—
Saturated hydrocarbons	49.0	29.6	3
Average mol. wt. of saturated hydrocarbons	18.2	21.0	50
Ethylene	25.2	17.1	—
Propylene	12.0	24.3	4
n-Butylene	2.9	9.0	35
Butadiene	2.0	6.6	18
Isobutylene	3.0	10.3	40
Amylenes and higher unsaturated hydrocarbons	—	2.5	—

Lewis-Dale[83] has isolated a monoalkylacetylene (probably ethyl- or isopropylacetylene), amylenes, benzene and toluene from the liquid hydrocarbons obtained in the compression of oil gas, i.e., illuminating gas made by the high temperature (about 1500° to 1700° F.) cracking of gas oils. Other unsaturated hydrocarbons were present, but as they readily polymerized their identification was impossible. This polymerization, resulting in the formation of a gummy, resin-like residue, renders difficult the production of a satisfactory motor fuel from the compression liquid.

CRACKED GASOLINE

The aim of commercially operated cracking processes is the production of lower boiling liquid hydrocarbons, usually those boiling within the gasoline range. The most important difference in composition between the synthetic cracked gasolines, produced by thermal degradation, and ordinary straight-run gasolines is the presence of considerable proportions of unsaturated hydrocarbons in the former and of traces only in the latter. The chemical composition of cracked gasoline depends upon a number of factors, most important of which are operating conditions (temperature, pressure, and duration of cracking) and the character of the charging stock.[83a] In a general way, the effect of increasing the temperature of cracking is to increase the percentage of unsaturated hydrocarbons in the cracked product. With increasing temperature of cracking, diolefins are produced in increasing proportions, and at still higher temperatures aromatic hydrocarbons are formed preponderatingly at the expense of the unsaturated hydrocarbons. Naphthenes (cyclopentane and cyclohexane derivatives) are present in considerable amount in most cracked gasolines made at lower temperatures, but at higher temperatures these largely undergo decomposition into aromatics. Relatively large proportions of paraffins are usually present in gasolines produced by cracking at low temperatures but at higher temperatures these are greatly reduced in quantity and vapor phase cracked gasolines generally contain smaller proportions of paraffin hydrocarbons. As might be expected, the character of the charging stock exerts considerable influence on the composition of the gasoline produced at low temperatures (i.e., in liquid phase operations) but at higher temperatures this effect is minimized by the occurrence of overwhelming secondary changes.)

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[83] *J.S.C.I.*, 1925, 44, 189T.

[83a] Analyses of gasolines obtained on cracking various petroleum oils are given by: Ionescu, *Bul. chim. soc. romane chim.*, 1930, 33, 37; *Chem. Abs.*, 1932, 26, 5407; Korovatzkii, *Neft. Khoz.*, 1932, 22, 217; *Chem. Abs.*, 1932, 26, 4456; Sager, *Petroleum*, 1933, 29 (15), 1; *Brit. Chem. Abs.* B, 1933, 452; Piguzov, *Acta Univ. Asiae Mediae (Tashkent)*, 1932, Ser. VI, No. 5; *Chem. Abs.*, 1933, 27, 4383.

The influence of increased pressure is to reduce the unsaturated hydrocarbon content of the cracked gasoline, probably by speeding up polymerization. However, this effect is reversed at still higher pressures, according to Frolich.[84] The pressure factor never exerts such a marked influence on the unsaturated content of the gasoline as does the temperature factor.

A large number of analyses of cracked gasolines produced from various charging stocks under various conditions have been published but it would be of little value to reproduce such analyses since in most cases the fundamental cracking conditions have been incompletely specified and the analytical methods employed are capable of yielding results only approximately accurate. Egloff[85] gave figures for the composition of various cracked gasolines from the Dubbs process showing that the unsaturated hydrocarbon content varies from 10 per cent to about 30 per cent and averages about 20 to 25 per cent. The proportions of the other three principal types of hydrocarbons appear to vary with the character of the charging stock, but the paraffins average 30 to 40 per cent and the aromatics about 20 per cent, although there may be wide deviations from these figures. According to Egloff,[86] the gasoline obtained by cracking a Californian kerosene under 14 to 21 atmospheres below 500° C. contained 17.3 per cent of olefins, 18.4 per cent of aromatics, 20 per cent of naphthenes, and 44.3 per cent of paraffin hydrocarbons. Garner[87] gave the composition for various liquid phase cracked gasolines shown in Table 30.

TABLE 30.—*Composition of Liquid Phase Cracked Gasolines.*

Source	Olefins	Aromatics	Naphthenes	Paraffins
	Per Cent			
High-pressure cracking of naphthene-base kerosene	24	9	35	32
Light gas oil *	30	8.5	15	46.5
Heavy gas oil *	41	6.5	9	43.5
Residue *	45	6	8	41

* From mixed base crude and cracked at 150 lbs. per sq. in.

The gasolines produced by *high temperature vapor phase cracking* are characterized by a higher content of unsaturated hydrocarbons (up to about 50 per cent) and aromatics, with only small amounts of paraffin hydrocarbons. For gasoline produced by vapor phase cracking in a Gyro unit, Wagner gave the composition, 45 to 50 per cent of olefins and diolefins and 40 to 45 per cent of aromatics, with the remainder naphthenes and only a trace of paraffins. The percentage of unsaturated hydrocarbons in vapor phase cracked gasolines does not usually exceed about 50 per cent, but distillates of such gasolines may have a higher unsaturated content.[88] A vapor phase cracked gasoline obtained by cracking light solar oil at a maximum temperature of 600° C. and a pressure of 100 pounds per square inch (contact time, 10 minutes) in a full-sized cracking still was found by Payne and Lowy[89] to possess the approximate composition: 35 per cent olefins, 17 per cent aromatics, 26 per cent naphthenes, and 22 per cent paraffins. The percentage of olefins was highest (over 40 per cent) in the fractions of this gasoline boiling below 100° C. and declined rapidly with rising boiling point.

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[84] *Chem. Met. Eng.*, 1931, **38**, 343.

[85] *Trans. Fuel Conference, World Power Conference, London, 1928*, 1929, 1, 763; *Chem. Abs.*, 1929, **23**, 4808.

[86] *Petroleum*, 1930, **26**, 1263; *Brit. Chem. Abs.* **B**, 1931, 187.

[87] *J. Inst. Pet. Tech.*, 1928, **14**, 710.

[88] Thus Garner (*J. Inst. Pet. Tech.*, 1928, **14**, 731) stated that a light aviation spirit, produced by the Lodge-Tinker vapor phase process, was found by him to have an olefin content of over 85%.

[89] *Ind. Eng. Chem.*, 1932, **24**, 432.

Very little work has been reported on the identification of pure saturated and unsaturated hydrocarbons in cracked gasolines. It is to be expected that the monolefins present in cracked products are principally of the branched-chain type, which are known to be more stable thermally than the corresponding straight-chain compounds. The diolefins in cracked gasolines made at higher temperatures appear to be conjugated unsaturated hydrocarbons both acyclic and cyclic, such as butadiene and its homologues, and cyclopentadiene. The naphthenes are mainly cyclopentane and cyclohexane derivatives (with a possible preponderance of the former type) but the presence of cyclobutane hydrocarbons is not improbable.

Brame and Hunter[90] conducted a very careful examination of the light fraction (boiling up to 120° C.) of a gasoline produced by cracking a Russian kerosene in a Cross cracking plant. The specific gravity of this fraction was reported as 0.751, and it contained 27.20 per cent unsaturated hydrocarbons, 4.97 per cent aromatic hydrocarbons, and 67.83 per cent (by difference) of saturated hydrocarbons. It was fractionated into eleven different fractions which were found to have the approximate compositions shown in Table 31.

Table 31.—*Composition of Fractions of Gasoline from a Russian Kerosene (Cross Process).*

Fraction ° C.	Unsaturates	Benzene	Toluene	Naphthenes	Paraffins
			Per Cent		
21°-45°	36	—	—	—	—
45°-57°	18	—	—	28.7	53.3
57°-68°	25	3.0	—	15.8	56.2
68°-76°	24	2.7	—	25.5	47.8
76°-85°	20	2.7	—	33.1	44.2
85°-94°	16	3.3	—	42.9	37.8
94°-99°	14	4.3*	—	41.0	40.7
99°-104°	20	2.1*	—	54.6	23.3
104°-110°	18	—	7.5	39.2	35.3
110°-112°	6	—	12.8	38.8	42.4
112°-120°	14	—	6.2	32.8	47.0

* As benzene and toluene.

By very careful fractionations and separation of the olefins as bromides, Brame and Hunter were able to obtain a sufficiently satisfactory separation of a number of hydrocarbons and identification of the following substances was regarded as being established:

Paraffins. Both paraffins and iso-paraffins were present including hexane, heptane, and the isohexanes, trimethylethylmethane and diisopropyl, with indications of pentane, isopentane, and isoheptanes.

Naphthenes. These occurred with the paraffins, being present in nearly equal amounts. Methylcyclopentane, cyclohexane, dimethylcyclopentane, and methylcyclohexane were isolated.

Olefins. These were the predominating unsaturated hydrocarbons in the lower-boiling fractions, and the presence of 3-, and 2-methylpentenes and of 4-, and 5-methylhexenes was probable. Olefins of the type $RCH{=}CH_2$ appeared to be absent. Cyclic olefins predominated in the unsaturated compounds in the higher-boiling fractions. Indications of the presence of *diolefins* were obtained in the first fractions with definite evidence of piperylene (1-methylbutadiene). Cyclic olefins (e.g., methylcyclopentene) predominated in the unsaturates boiling from 90° to 120° C.

Aromatics. Small percentages of aromatics, considered as benzene and toluene, were present in the gasoline investigated.

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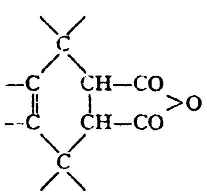
[90] *J. Inst. Pet. Tech.*, 1927, 13, 794.

Ivanov[90a] analyzed a cracked gasoline, boiling between 20° and 150° C. He found that 25 per cent of the fraction boiling from 60° to 70° C. and 40 per cent of the fraction boiling at 120° to 125° C. consisted of unsaturated n- and iso-hydrocarbons. About 30 per cent of the gasoline was naphthenes. He was also able to show that 3-hexene, 1- and 2-heptene, 3-octene, benzene, toluene and xylenes were present.

It is interesting to note that Payne and Lowy[91] inferred the probable presence of methylcyclobutane in a fraction, boiling at 29.4° to 35.0° C., of a vapor phase cracked gasoline. The variation in the unsaturated hydrocarbon content of this cracked gasoline with the boiling point of its various fractions before and after a second heat treatment (at 300° C. and 68 atmospheres for 6 hours in a steel bomb) was shown.

Birch and Scott[92] recorded the results of an investigation of the conjugated diolefins present in a vapor phase cracked gasoline, making use of the reaction of such hydrocarbons with maleic anhydride to form, in many instances, crystalline derivatives[93] of the type,



Butadiene, piperylene, isoprene and cyclopentadiene were all present in the lower boiling fractions of this gasoline and could be readily separated and identified. Attempts to isolate the corresponding derivatives from the dimethylbutadiene fraction of the gasoline were unsuccessful, probably on account of the complex nature of the fractions examined.

Markovich[94] described the results of a careful rectification of the lower-boiling liquid and volatile products from cracking crude oil in the vapor phase at high temperatures ("blau" gas cracking). The compression product consisted of 2 per cent of propylene, 19 per cent of butylenes, 28 per cent of C_5 hydrocarbons (up to 90 per cent unsaturates), 22 per cent of C_6 hydrocarbons (up to 85 per cent unsaturates), 17 per cent of benzene, 12 per cent of higher hydrocarbons, and some butadiene and butane.

[90a] *J. Appl. Chem., Russ.*, 1933, **6**, 257; *Brit. Chem. Abs.* **B**, 1933, 691.

[91] *Ind. Eng. Chem.*, 1932, **24**, 432.

[92] *Ind. Eng. Chem.*, 1932, **24**, 49.

[93] The formation of these crystalline condensation products was described by Diels and Alder (*Ann.*, 1928, **460**, 98; 1929, **470**, 101; 1929, **476**, 102); see also Farmer and Warren, *J.C.S.*, 1929, 897; I. G. Farbenindustrie A.-G., British Patent 352.164, 1931; see Chapter 27.

[94] *Neft. Khoz.*, 1929, **16**, 67; *Brit. Chem. Abs.* **B**, 1930, 130.

Chapter 4

Production of Unsaturated Hydrocarbons by Pyrolysis—Olefins, Acetylene and Diolefins

The action of heat on various saturated hydrocarbons frequently yields unsaturated compounds and in certain instances leads to rearrangements within the molecules. The mechanism of these reactions has not been definitely established. Nevertheless, Dunstan, Hague and Wheeler[1] have concluded, from a consideration of their work on paraffin hydrocarbons ranging from ethane to hexane, that the primary decompositions are represented by the rupture of the chain at any point, with the simultaneous production of an olefin and the complementary lower paraffin, or (as a limiting case) hydrogen. The tendency to eliminate hydrogen, they found, decreases as the size of the molecule increases. They also stated that the main primary reactions common to ethylene, propylene and the butylenes involve the formation of olefins of either two or four carbon atoms or both. Ebrey and Engelder,[2] from their investigations of the pyrolysis of propane, have also shown that a carbon-to-carbon linkage breaks more readily than a carbon-to-hydrogen linkage. From his work on the cracking of Rangoon paraffin in the vapor phase, Heymans[3] concluded that cracking occurs at the end of the hydrocarbon chain and then proceeds from point to point along the chain. These primary decomposition reactions are followed generally by purely synthetic reactions occurring under the action of heat and resulting in the formation of hydrocarbons of increased molecular weights, such as those of the aromatic series.

From these considerations it is seen that maximum yields of olefins and diolefins require careful regulation of the conditions of cracking to prevent change or degradation of the unsaturated hydrocarbons first formed. The following account will discuss first the formation of the individual olefins from various raw materials, and later the pyrolytic production of acetylene and the diolefins. The latter are important as possible starting materials for the synthesis of rubber substitutes, an account of which will follow in Chapter 26.

ETHYLENE

Ethylene is an important product of the cracking of hydrocarbons, even of methane. It occurs in the gases produced in the commercial cracking of petroleum oils. Low temperature cracking (in the liquid phase) at about 480° C. yields a gas comparatively poor in olefins. Of the olefins thus formed propylene seems to be the most important constituent. Generally, the ethylene content of liquid phase cracking gas does not exceed 5 per cent. On the other hand, high temperature vapor phase cracking yields a gas relatively rich in olefin hydrocarbons, of which ethylene is predominant. High temperature cracking at about 600° to 650° C. normally yields a gas containing 50 per cent or more of unsaturated hydrocarbons of which about 25 per cent is ethylene. Large quantities of ethylene will become available with the wider adoption of vapor phase cracking for the manufacture of motor fuels with high antiknock value.

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[1] *J.S.C.I.*, 1931, **50**, 313T.

[2] *Ind. Eng. Chem.*, 1931, **31**, 1033.

[3] *J. Inst. Pet. Tech.*, 1930, **16**, 661; *Chem. Abs.*, 1931, **25**, 1066.

Ethylene may be obtained also by the controlled pyrolysis of the paraffin hydrocarbons of natural gas and light gasoline. The researches of numerous workers in this field have shown that the lower paraffin hydrocarbons containing from 2 to 5 carbon atoms are especially suitable for the pyrolytic preparation of ethylene. At the high temperatures necessary for the pyrolysis of methane (1000° C. and higher), ethylene is largely converted into aromatic hydrocarbons and other substances. Thus, Stanley and Nash[4] reported that only 1 to 2 per cent of ethylene and 2 to 3 per cent of acetylene were obtained by the pyrolysis of methane at 1100° to 1150° C. The yield of acetylene increased with rising temperatures of pyrolysis but lower temperatures appeared necessary for larger production of ethylene. Probably the best temperature for the conversion of methane into ethylene is in the range of 1050° to 1100° C.

According to de Rudder and Biedermann,[5] the maximum yield of ethylene from methane, namely 4 per cent of the gaseous products, is obtained by pyrolysis at 1200° C. under 100 mm. pressure. The gas obtained under these conditions also contains 2.5 per cent acetylene. The results of Frolich, White and Dayton[6] on the pyrolysis of methane under reduced pressure in silica tubes at temperatures above 1000° C. showed that the percentage of ethylene in the reaction gases is at a maximum of almost 2 per cent at about 1100° C. under 33 to 102 mm. pressure, and that the pressure or time of contact exerts little influence on this value. Padovani and Magaldi[7] reported that in the pyrolysis of methane at 1000° to 1250° C. in silica tubes, dilution with hydrogen increases the formation of ethylene and acetylene at lower rates of flow, although the effect is reversed at higher rates. On the other hand, Smith, Grandone and Rall[8] found that the percentage of ethylene and acetylene in the gaseous reaction products was increased by dilution of the methane with either hydrogen or nitrogen. Warren[9] investigated the influence of pressures higher than atmospheric on the percentage of total unsaturated hydrocarbons in the gaseous products when pyrolysis was conducted in silica tubes. Temperatures of 902° to 1122° C. and pressures as high as 104 atmospheres were employed. The yield of unsaturated hydrocarbons was found to diminish with increasing pressure. Storch[10] examined the pyrolysis of methane with carbon filaments at 1457° to 2000° C. in bulbs cooled by liquid nitrogen and at —183°, —78°, and 0° C. A 95 per cent yield of ethane is found with liquid nitrogen, at —183° C. ethylene and acetylene are produced, and at higher temperatures the products are carbon and hydrogen.

It appears, therefore, that only relatively small yields of ethylene may be obtained by the pyrolysis of methane with short heating periods in the temperature range of 1050° to 1200° C. Under these conditions acetylene and other products are formed at the same time. At higher temperatures, acetylene predominates. Inactive heating surfaces (consisting of materials such as silica, porcelain or copper, which do not accelerate the decomposition of methane into its elements) are essential for optimum yields of unsaturated hydrocarbons. The use of gaseous diluents also seems to be advantageous. In view of the high temperatures necessary and the relatively poor conversions obtainable, methane is not a promising material for the production of ethylene.

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[4] *J.S.C.I.*, 1929, **48**, 1T.

[5] *Compt. rend.*, 1930, **190**, 1194; *Bull. soc. chim.*, 1930, (4) **47**, 704; *Chem. Abs.*, 1930, **24**, 4255; *Brit. Chem. Abs.* **A**, 1930, 887, 1268.

[6] *Ind. Eng. Chem.*, 1930, **22**, 20.

[7] *Atti III congresso naz. chim. pura applicata*, 1930, 730; *Chem. Abs.*, 1931, **25**, 3309; *Brit. Chem. Abs.* **A**, 1931, 1030.

[8] *U. S. Bureau Mines Repts. Investigations*, **3143**, 1931; *Chem. Abs.*, 1932, **26**, 279.

[9] *Canadian Dept. Mines, Mines Branch Rept.*, **725-1**, 1932, 15; *Chem. Abs.*, 1932, **26**, 5399.

[10] *J.A.C.S.*, 1932, **54**, 4188.

Ethane is an almost ideal raw material for the pyrolytic production of ethylene. The decomposition of ethane at 675° C. to ethylene and hydrogen was observed by Bone and Coward.[11] The reaction involved, namely,

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

was studied by Pease and Durgan[12] at temperatures of 600° to 700° C. and shown to be reversible and complicated to some extent by other reactions, such as the formation of methane. They obtained values of the equilibrium constant, K, at 600°, 650° and 700° C.

$$K = \frac{[C_2H_4][H_2]}{[C_2H_6]}$$

Frey and Huppke[12a] measured the same equilibrium at temperatures of 400° to 500° C., using air-dried chromic-oxide gel as a catalyst. The values of K obtained by the latter investigators, as well as those by Pease and Durgan, are given below:

Temp. ° C.	400°	450°	500°	600°	650°	700°
K	0.00015	0.00076	0.0032	0.031	0.082	0.20

Cambron[13] passed ethane over an electrically heated carbon rod at 989° C. and found that 50.5 per cent of the entering gas was converted to ethylene and 90 per cent of the ethane decomposing did so according to the above equation.

Elworthy[14] reported that a commercial process has been developed for converting ethane (separated from natural gas by fractionation) into ethylene by cracking in copper, earthenware, or porcelain tubes at about 600° C. The temperatures might possibly be raised at sufficiently high gas velocities (i.e., short heating periods). The occurrence of undesirable side reactions becomes more marked as the temperature is increased. Hague and Wheeler[15] reported, however, that even at 700° C. in the presence of silica heating surfaces about 90 per cent of the decomposed ethane was dehydrogenated to form ethylene, and that the reaction gas contained 21.3 per cent of ethylene and only 2.7 per cent of methane. The ethylene content of the gaseous products of the pyrolysis of ethane was at a maximum of 24.3 per cent in an experiment at 750° C., but the gas also contained 13.3 per cent of methane and 4.7 per cent of higher olefins. This indicated that the efficiency of ethylene production from ethane was lower at 750° C. than at 700° C. In order to limit other reactions, such as the formation of methane, it appears necessary to employ short heating periods at temperatures not above 800° C., dehydrogenating in one passage.

The usual metallic dehydrogenating catalysts (finely divided copper or nickel) might be expected to assist in the conversion of paraffins to olefins. Indications are, however, that although these materials greatly reduce the temperature required for the reaction, they simultaneously catalyze the formation of methane, carbon and hydrogen. Thus, the efficiency of olefin formation is reduced and little advantage apparently accrues from their use. Elworthy[16] found, for example, that when a gas containing 80 per cent of methane and 7 per cent of ethane was passed through tubes containing a catalyst composed of copper oxide, pumice and carbon, the proportion of olefin in the gaseous products was very low. He concluded that the olefin was formed only from ethane. The best temperature for the reaction was about 800° C. The dehydrogenation of ethane was accelerated by the presence of reduced copper, and a molybdenum trioxide coating on copper bronze was also active.[17]

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[11] *J.C.S.*, 1908, **93**, 1197.

[12] *J.A.C.S.*, 1929, **50**, 2715.

[12a] *Ind. Eng. Chem.*, 1933, **25**, 54.

[13] *Can. J. Research*, 1932, **7**, 646; *Chem. Abs.*, 1933, **27**, 1483.

[14] *Industrial Chemist*, 1928, **4**, 275. This is stated to be the process developed by the Carbide and Carbon Chemicals Corp.

[15] *J.C.S.*, 1929, 378.

Matignon, Kling and Florentin[18] observed that the dehydrogenation of the lower paraffins in the presence of catalysts of pumice impregnated with copper and nickel is favored by low reaction temperatures and short periods of contact. Thus, the exposure of ethane to the action of a nickel-pumice catalyst at 600° C. yielded reaction gases of the following compositions:

Contact Time	Analysis of Reaction Gas	Per Cent by Volume		
Secs.	C_2H_4	H_2	C_2H_6	CH_4
42	14.2	22.0	51.0	12.8
396	12.7	40.7	0.0	49.9

As the molecular weight of the paraffin hydrocarbon increases, there is a greater tendency to pyrolysis into olefins and paraffins of lower molecular weight and the simple dehydrogenation reaction, forming an olefin of the same number of carbon atoms as the original paraffin, is increasingly obscured. Thus, propane undergoes pyrolysis in contact with silica to form methane, ethylene, propylene and hydrogen. According to Schneider and Frolich,[19] in the pyrolysis of propane at 725° C. under atmospheric pressure with short periods of heating (so that 20 to 40 per cent of the propane is decomposed per passage), about 50 per cent of the hydrocarbon decomposed is converted into methane and ethylene according to the reaction

$$C_3H_8 \longrightarrow CH_4 + C_2H_4,$$

and about 40 per cent is dehydrogenated to propylene. Using n-butane, Hague and Wheeler[20] observed that at 650° C. in the presence of silica about 43 per cent of the hydrocarbon decomposed follows the reaction,

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2,$$

36 per cent forms methane and propylene, and 21 per cent is converted to hydrogen and butylene.

In the pyrolysis of these paraffin hydrocarbons considerable ethylene is formed together with propylene and its homologues. The cracking of butane and isobutane is now carried out on a commercial scale for producing a mixture of ethylene and propylene, used in the manufacture of glycols.[21]

Von Piotrowski and Winkler[22] made a special study of the optimum conditions of pyrolysis to olefins of a propane-butane mixture and of a stripped Boryslaw (Poland) natural gas. From the propane-butane mixture (39 per cent propane, 50 per cent butane, and 11 per cent pentane), the yield of olefins with

[16] *Trans. Royal Soc. Canada*, 1922, **16**, III, 105; *Chem. Abs.*, 1923, **17**, 2042.

[17] Cambron, *Can. J. Research*, 1932, **7**, 646; *Chem. Abs.*, 1933, **27**, 1483.

[18] *Compt. rend.*, 1932, **194**, 1040; *Brit. Chem. Abs.* **A**, 1932, 495.

[19] ***Ind. Eng. Chem.***, 1931, **23**, 1405.

[20] *Loc. cit.*

[21] For the manufacture of glycols, see Chapter 22.

[22] *Przemysl Chem.*, 1930, **14**, 49, 83; *Petroleum Z.*, 1930, **26**, 763; *Chem. Abs.*, 1930, **24**, 4924; *Brit. Chem. Abs.* **B**, 1930, 309, 850.

more than two carbon atoms was highest at 730° C., and that of the ethylene reached a maximum at about 800° C. The heating period was about 8 seconds, and the conversion to olefins amounted to 70 per cent or more.

According to Smolenski,[23] the pyrolysis of crude naphtha at 600° C. yielded 15 cubic meters of gaseous olefins per 100 kilograms of naphtha, their concentration in the crude cracking gas being 35 to 37 per cent. At 700° C. the olefins formed (mainly ethylene) corresponded to 15 kilograms per 100 kilograms of naphtha (concentration in the gas being 20 to 22 per cent).

Large scale experiments on the production of both aromatic hydrocarbons and ethylene by the pyrolysis of various gaseous mixtures of paraffins (mainly propane and butanes) have been described by Podbielniak.[24] His results clearly show the practicability of using these gaseous hydrocarbons as raw materials for the manufacture of ethylene. Pyrolysis was effected in a plant capable of handling about 25,000 cu. ft. of gas per day. In the treatment of hydrocarbon gases rich in propane and butanes, e.g., stabilizer gas, the optimum temperature for the production of aromatic hydrocarbons was 1650° to 1700° F. (900° to 925° C.), and the maximum yield of ethylene was obtained at 1500° to 1550° F. (815° to 845° C.). By careful control of operating conditions, special alloy metal reaction tubes could be used for either reaction. The results of two large scale tests on the manufacture of ethylene from gaseous paraffins are summarized below:

Composition of Raw Gas Per Cent by Volume				Outlet Temp. of Cracked Gas, ° F.	Expansion Ratio of Cracked to Raw Gas	Per Cent C_2H_4 in Cracked Gas
CH_4	C_2H_6	C_3H_8	C_4H_{10}			
1.7	9.5	76.2	10.0	1,550°	1.709	26.8
2.2	10.2	—	87.6	1,525°	1.520	26.0

For maximum yields of ethylene, recycling the reaction products after the removal of the ethylene is particularly advantageous. On the assumption that ethylene is removed after each stage of pyrolysis and that propylene and heavier hydrocarbons are recycled through the furnace, Podbielniak calculated from the data of the second experiment in the preceding table that the total volume of ethylene obtainable from 1000 cu. ft. of gas in five successive passages through the furnace is about 636.6 cu. ft., made up as follows:

	Cu. Ft. of Ethylene from 1000 Cu. Ft. of Raw Gas
First Passage	395
Second Passage	152
Third Passage	58.5
Fourth Passage	22.5
Fifth Passage	8.6
Total	636.6

In the course of an investigation of the effect of time and temperature upon the cracking of a representative Mid-Continent gas oil, Geniesse and Reuter[25] determined the yields of ethylene and other unsaturated gaseous hydrocarbons produced at various temperatures and at different periods of contact. The gas oil was pyrolyzed in the vapor phase in reaction chambers of pyrex glass. Some of the results of these investigators are given in Table 32.

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[23] *Przemysl Chem.*, 1927, 11, 146; *Chem. Abs.*, 1929, **23**, 2929.
[24] *Oil and Gas J.*, 1931, **29** (52), 22.
[25] *Ind. Eng. Chem.*, 1930, **22**, 1274.

TABLE 32.—*Effect of Temperature and Time of Contact on the Yield of Ethylene and Other Gaseous Unsaturated Hydrocarbons.*

Temperature ° C.	600°	625°	640°	640°	640°	640°	640°	640°	700°	700°
Cracking Conditions:										
(a) Time of contact, min. . . .	0.125	0.102	0.013	0.022	0.051	0.063	0.081	0.39	0.023	0.065
(b) Time-temperature index*.	16.5	40	8.6	15	35	44	56	270	185	560
Yield of Gas:										
% by weight of oil cracked	22.5	39.3	11	18	29.3	37.5	43	59	65.5	66.6
Gas:										
(a) Density	1.06	1.03	1.03	1.01	1.08	1.04	1.10	1.02	—	1.10
(b) Hydrogen, % by volume. .	6.1	7.0	5.1	7.5	6.0	12.1	7.1	7.9	8.5	9.9
(c) Ethylene, % by volume . .	23	24	27	26	25	23	24	20	28	25
(d) Total unsaturated hydrocarbons, % by volume . .	56	55	57	57	59	59	58	50	58	54

* The time-temperature index is defined by the expression $\left(2^{\frac{T-480}{17}}\right) \times t$, in which *T* is the cracking temperature in °C. and *t* the time in minutes. (See also Chapter 3.)

It will be seen from the table that the greatest ethylene production was obtained at 700° C., the highest temperature reported. With a contact period of 0.023 minute at 700° C., gas oil yielded 65.5 per cent by weight of gaseous products containing 28 per cent by volume of ethylene, corresponding to an overall conversion of gas oil into ethylene, of about 17 per cent by weight per passage.

To transform saturated hydrocarbons and petroleum distillates into ethylene, higher temperatures are required than when propylene and the butylenes are the desired products. A review of pyrolytic processes for making olefins indicates that the raw materials generally employed are gaseous paraffin hydrocarbons (e.g., coke-oven gas or natural gas) or the higher boiling petroleum fractions.

In the products from cracking paraffin oils, Tichy[26] found both unsaturated and aromatic hydrocarbons. With the aid of metallic oxide and chloride catalysts (the best being aluminum chloride and stannic oxide), the decomposition time was decreased by one-half and the yields of low boiling fractions were increased.

Unsaturated aliphatic hydrocarbons, such as ethylene and acetylene, may be produced from paraffin hydrocarbons, especially from methane, by passing the latter over catalysts, e.g., salts or hydroxides of the alkaline earth metals, magnesium, or beryllium, compounds of selenium, tellurium, or thallium, or activated carbon or silica, at temperatures of 700° to 1000° C. A sufficiently rapid rate of flow should be used to preclude further condensation of the initial products to aromatic hydrocarbons.[27] If the gaseous products are quickly removed from the reaction zone, acetylene is said to be the principal product at very high temperatures and ethylene at somewhat lower ones. By arranging the materials in the reaction chamber to form straight channels of uniform cross-sections, irregularities in gas velocity, which result in carbon deposition, are avoided.[27a]

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[26] *Paliva a Topeni*, 1929, **11**, 85, 100; *Chem. Abs.*, 1930, **24**, 4925.
[27] I. G. Farbenindustrie A.-G., British Patent 264,827, 1927; *Brit. Chem. Abs.* **B**, 1928, 327.
[27a] I. G. Farbenindustrie A.-G., British Patent 366,549, 1930; *Chem. Abs.*, 1933, **27**, 1889.

Folliet[28] converted methane into ethylene and other olefins to the extent of 80 per cent by heating a thin stream of the gas (to secure uniform temperature) to 950° C. followed by sudden cooling to atmospheric temperature. The pressure in the apparatus was maintained at 20 mm.

Ethane fractionated from natural gas was used by Haynes and Curme[29] as the raw material for the production of ethylene by pyrolysis at temperatures above 500° C. Haynes and Curme[30] later extended this process to the making of other olefins. The individual gaseous paraffins are prepared in a state of substantial purity by fractional condensation and rectification of natural gas, and are subjected separately to heat treatment under the optimum conditions for conversion to olefins. The products of thermal decomposition are combined, and from this mixture at least one of the paraffins originally treated, e.g., ethane or propane, is isolated by fractionation for reuse in a subsequent heat-treatment.

The separation of ethylene from ethane in the gases from coal distillation can be effected by absorbing ethylene in sulphuric acid.[31] The residual ethane is subjected to pyrolysis to yield ethylene and hydrogen, the ethylene being recovered by solution in the acid.

An unusual method for making ethylene from methane is described by Agnus,[32] who passed carbon disulphide and methane over heated pumice or activated carbon and substances which combine with sulphur, such as copper or zinc.

According to van Peski,[33] propane may be converted into a mixture of ethylene and methane by passing it over granulated calcium, iron or tungsten carbide at 600° to 800° C. The catalyst remained active for several days. Molybdenum mixed with pumice catalyzes the decomposition of propane to methane and ethylene still more rapidly. Evidently carbides and molybdenum on pumice exert a selective catalytic influence on the reaction,

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$

which is merely one of the several modes of decomposition of propane by heat treatment. A gas oil, boiling at 220° to 340° C., when treated in this manner yielded a gas containing a large proportion of unsaturated hydrocarbons and a liquid condensate boiling between 60° and 180° C.

The pyrolysis of cracked petroleum fractions solely by superheated steam under pressure has been proposed by Fenton.[34] Subjecting tar oils, having a boiling point of 250° C. and higher, to destructive distillation at temperatures between 800° and 900° C. in the presence of steam produces gases of high olefin content (40 to 50 per cent).[35] The predominating olefinic constituent is ethylene, of which 88 to 90 per cent can be recovered by passing the gases once through activated charcoal. Suida[36] described a similar process in which gases rich in olefins are obtained by the destructive distillation of crude tar in the presence of steam.

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[28] British Patent 261,267, 1926; assigned to Pétrole synthétique soc. anon.; *Brit. Chem. Abs.* **B**, 1927, 100.

[29] U. S. Patent 1,460,545, July 3, 1923; assigned to Linde Air Products Co.; *Chem. Abs.*, 1923, 17, 2886.

[30] U. S. Patent 1,524,355, Jan. 27, 1925; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1925, 19, 991. *Cf.* Canadian Patent 245,154, 1924; *Chem. Abs.*, 1925, 19, 657.

[31] Compagnie de Béthune, British Patent 303,176, 1928; *Brit. Chem. Abs.* **B**, 1930, 358. Absorption of ethylene in sulphuric acid to produce ethyl alcohol and other substances is discussed in Chapter 12.

[32] French Patent 648,340, 1927; *Chem. Abs.*, 1929, 23, 2989.

[33] British Patent 315,193, 1928; *Brit. Chem. Abs.* **B**, 1929, 770. German Patent 572,203, 1928, *Chem. Abs.*, 1933, 27, 2960.

[34] U. S. Patent 1,394,481, Oct. 18, 1921; *Chem. Abs.*, 1922, 16, 488. See also U. S. Patent 1,396.174, Nov. 8, 1921; *Chem. Abs.*, 1922, 16, 642.

[35] Chem. Fabrik vorm. Weiler-ter Meer, British Patent 237,415, 1924; *J.S.C.I.*, 1925, 46, 748B.

[36] British Patent 225,546, 1924; *J.S.C.I.*, 1925, 46, 491B.

PROPYLENE

The gases from commercial cracking operations contain appreciable proportions of propylene, which is being utilized for the manufacture of isopropyl alcohol and other products.[37] In the gases from low temperature (liquid phase) cracking, propylene appears to be the main olefinic constituent, although the actual percentage is not normally very high (maximum about 10 per cent). In high temperature (vapor phase) cracking the actual percentage of propylene is somewhat increased, but this gas is associated with a much greater proportion of ethylene. According to Wagner,[38] a typical liquid phase cracking gas (Cross process) contains 5.3 per cent of propylene and, the gas from a vapor phase cracking (Gyro) process has a propylene content of 18.1 per cent.

Although propylene is an important product of the pyrolysis of many petroleum distillates and higher hydrocarbons, temperatures somewhat lower than those used in making ethylene are required for its manufacture, on account of the greater tendency of propylene to undergo decomposition with the formation of, among other substances, ethylene itself. No precise information on this matter appears to be available but temperatures of about 600° C. seem to be the most favorable for the pyrolysis of petroleum oils to propylene. Thus, according to Dobryanski, Arkhangelski and Stepanyan,[39] who investigated the pyrolysis of various petroleum fractions in a copper tube at 550° to 750° C., the highest yields of propylene were obtained from solar oil at temperatures of 600° to 650° C. Above this range there was a tendency for the propylene to undergo decomposition. Moreover, the yield of propylene was not increased by using either nickel or iron as catalysts. Under the best conditions 100 grams of solar oil (initial boiling point, 305° C.) gave about 13 grams of propylene.

The obvious starting material for making propylene is propane, but Hague and Wheeler[40] and others have shown that this hydrocarbon can decompose during pyrolysis in at least two ways:

$$(1)\quad CH_3CH_2CH_3 \longrightarrow CH_4 + CH_2{=}CH_2 \text{ (demethanation)}$$

$$(2)\quad CH_3CH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + H_2 \text{ (dehydrogenation)}$$

The first reaction, yielding methane and ethylene, was found by Hague and Wheeler to occur to the extent of about 60 per cent (calculated on the propane decomposed) at 700° C. in silica tubes and the second, forming propylene and hydrogen, to the extent of nearly 40 per cent. At temperatures above 700° C. secondary changes begin to intervene.

Ebrey and Engelder[41] observed that the pyrolysis of propane in silica tubes gives varying proportions of hydrogen, methane, ethane, ethylene and propylene and that the proportion of hydrogen increases with rising temperature. Unsaturated hydrocarbon formation reached a maximum at 770° C. Catalysts containing nickel, cobalt, chromium, or iron increased the proportion of hydrogen and methane formed.

It has been shown further by Schneider and Frolich[42] that the relative extents to which dehydrogenation and demethanation reactions proceed during the pyrolysis of propane (at 725° C. under atmospheric pressure in silica tubes) are practically the same for all degrees of propane decomposition from zero to about 40

[37] For the preparation of isopropyl alcohol see Chapter 14.
[38] *Refiner,* 1930, 9 (6), 70; *Chem. Abs.*, 1930, 24, 5142.
[39] *Neft. Khoz.*, 1928, 15, 46; *Chem. Abs.*, 1929, 23, 3800.
[40] *J.C.S.*, 1929, 378.
[41] *Ind. Eng. Chem.*, 1931, 23, 1033.
[42] *Ind. Eng. Chem.*, 1931, 23, 1405.

per cent. In the non-catalytic pyrolysis of propane, ethylene is always produced in amounts in excess of propylene even at short times of contact when only a small quantity of the propane is decomposed.

The possibility of selectively accelerating dehydrogenation at the expense of demethanation is indicated by the work of Boeckler.[43] He observed that the production of propylene was greatly increased by using a catalyst consisting of 78.5 molar per cent zinc and 21.5 molar per cent chromium. With this catalyst a larger yield of propylene was obtained at 655° C. than without it at 730° C., even though the rate of flow of gas at the latter temperature was one-fourth that at 655° C. At temperatures as low as 520° C., propane diluted with 67 per cent of nitrogen yielded 11 per cent propylene. Matignon, Kling and Florentin[44] reported that in the presence of a catalyst of pumice impregnated with copper the decomposition of propane at 500° C. yields only a negligible proportion of ethylene. The formation of propylene is favored at all temperatures by short times of contact with the heated catalyst. With prolonged periods of contact, methane and ethylene become the main reaction products.

The results of von Piotrowski and Winkler[45] on the pyrolysis of a stripped Boryslaw natural gas containing propane and methane in the volume proportions of 22 to 78 appear to indicate that almost quantitative conversion of propane into propylene can be achieved at about 780° C. with a contact period of 11 seconds in the presence of an excess of methane as a diluent. It is to be expected, from purely theoretical considerations, that dilution of propane with excess methane should favor the formation of propylene, since such dilution would tend to suppress the demethanation reaction.

In most thermal decompositions the propylene formed is mixed with other olefinic gases. The yield of this olefin increases with rising temperature up to a certain point, above which it falls off and ethylene becomes the predominant olefin in the cracking gas.

Haynes and Curme[46] subjected propane, which has been separated in substantially pure form from a gaseous mixture containing it, to pyrolysis under optimum conditions for dehydrogenation to propylene. Propane and propylene are isolated from the reaction products, and the propane returned to the pyrolysis cycle.

Heinemann[47] has described a method for the manufacture of propylene by the direct combination of methane with acetylene, according to the reaction,

$$C_2H_2 + CH_4 \longrightarrow C_3H_6$$

The process involves the passage of equal volumes of methane and acetylene through tubes containing such contact materials as copper wool, copper gauze, aluminum or magnesium turnings coated with a metal like platinum, or a copper-platinum-pumice catalyst. The temperature ranged from 100° to 200° C., depending upon the catalyst employed. The use of inert gaseous diluents, as for example carbon dioxide or nitrogen, is advantageous. The yield of propylene is said to be approximately 78 per cent.

According to Ellis,[48] fractions of casinghead gasoline consisting principally of pentane may be cracked to yield gaseous olefins, advantageously in the presence of catalysts of nickel, copper, or brass. At about 720° C., a pressure of about 0.5 atmosphere, and a gas velocity of 3 to 40 cu. ft. per hour per sq. in. of cross-sectional area of the cracking tube, a 32.8 per cent yield of olefins, chiefly propylene, was obtained. Ethylene was formed to the extent of 9.6 per cent.

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[43] Thesis, Mass. Inst. Tech., 1929; mentioned by Egloff, Schaad and Lowry, *J. Phys. Chem.*, 1930, **34**, 1685.

[44] *Compt. rend.*, 1932, **194**, 1040; *Brit. Chem. Abs.* **A**, 1932, 495.

[45] *Przemysl Chem.*, 1930, 14, 49, 83; *Petroleum Z.*, 1930, **26**, 763; *Brit. Chem. Abs.* **B**, 1930, 309, 850; *Chem. Abs.*, 1930, **24**, 4924.

[46] Canadian Patent 245,154, 1924; *Chem. Abs.*, 1925, **19**, 657.

[47] U. S. Patent 1,134,677, Apr. 6, 1915; *Chem. Abs.*, 1915, **9**, 1369.

[48] U. S. Patent 1,594,823, Aug. 3, 1926; assigned to S. B. Hunt, Trustee; *Brit. Chem. Abs.* **B**, 1926, 898.

Propylene was made by the pyrolysis of butane or isobutane in the presence of a catalyst, such as copper, at 700° C. by Gerstmyer and Clayton.[49] Best results were secured when the rate of gas flow was such that the expansion ratio of the inlet to exit gases was about 1 to 1.29.

BUTYLENES AND HIGHER OLEFINS

Butylenes are produced to a considerable extent in commercial cracking. Low temperature cracking yields a gas containing about 4 per cent of butylenes and the butylene content of vapor phase cracking gas varies from 5 to 9 per cent. It is known that all three butylenes are present in cracking gas but the relative proportions of these isomers apparently has not been determined. According to Wagner[50] large quantities of isobutylene and somewhat smaller amounts of butadiene are produced by vapor phase processes.

The direct thermal dehydrogenation of n-butane to 1-butene is apparently not a satisfactory method for the manufacture of this olefin. Hague and Wheeler[51] and Hurd and Spence[52] have found that dehydrogenation takes place to a small degree, but that reactions involving the splitting of the molecule predominate. According to Hurd and Spence, the thermal dehydrogenation of isobutane to isobutylene is an important reaction in the region of 600° to 700° C., at which temperatures methane and propylene are formed simultaneously.

PRODUCTION OF MIXTURES OF GASEOUS OLEFINS

The increasing value of the lower olefins in organic synthesis has stimulated interest in their production and much activity has been displayed in their utilization.[53] Bowen[54] discussed their importance in the manufacture of such products as ethyl, isopropyl, secondary and tertiary butyl and amyl alcohols; ethylene glycol; ethers, esters and ketones derived from these alcohols; triethanolamine; and synthetic lubricating oils. The methods of making these compounds and their uses are discussed in succeeding chapters.

As raw materials for the pyrolytic preparation of olefins and olefin mixtures, bituminous coal, gaseous paraffin hydrocarbons, and petroleum distillates have been investigated. The use of lower paraffin hydrocarbon gases, or mixtures which contain them, has attracted attention because of their abundance and relative cheapness. Large quantities of propane and butanes, obtained as by-products from the stabilization of natural-gas gasoline, are available and would appear to be ideal starting materials for making olefins, particularly ethylene and propylene.

In this connection the investigations of von Piotrowski and Winkler[55] on the pyrolysis of saturated gaseous hydrocarbons is of interest. The furnace employed in their work consisted of a double reaction tube heated in a bath of molten lead, the ingoing gases being preheated in the inner reaction tube and cracked in the outer one. From a mixture of propane (39 per cent), butanes (50 per cent) and pentanes (11 per cent) at an optimum contact time of about 8 seconds, the yield of unsaturated gaseous hydrocarbons having more than two carbon atoms was a maximum at 730° C. The optimum temperature for ethylene formation was 800° C. Temperatures of 700° to 760° C. gave the highest total yields of unsaturated gaseous hydrocarbons.

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[49] U. S. Patent 1,871,786, Aug. 16, 1932; assigned to Columbia Engineering and Management Corp.; *Chem. Abs.*, 1932, **26**, 5971.

[50] *Refiner*, 1930, **9** (6), 70; *Chem. Abs.*, 1932, **26**, 5142.

[51] *J.C.S.*, 1929, 386.

[52] *J.A.C.S.*, 1929, **51**, 3355.

[53] See *Chem. Met. Eng.*, 1929, **36**, 399.

[54] *Oil and Gas J.*, 1932, **30** (46), 88, 166; *Chem. Abs.*, 1932, **26**, 6106.

[55] *Przemysl Chem.*, 1930, **14**, 49, 83; *Petroleum Z.*, 1930, **26**, 763; *Brit. Chem. Abs.* **B**, 1930, 309, 850; *Chem. Abs.*, 1930, **24**, 4924.

Frey and Hepp[55a] cracked butane, isobutane, pentane, isopentane, 2,2-dimethylpropane, hexane and 2,3-dimethylbutane at 400° to 575° C. The primary products of decomposition are methane and an olefin, or a paraffin and an olefin, or two olefins and hydrogen.

The work of Podbielniak[56] on cracking gaseous paraffins, such as propane-butane mixtures, has been previously noted. It need only be mentioned again that, in cracking for maximum yields of olefins, Podbielniak stressed the advantages of recycling the gases after removing the olefins formed during each cycle. For example, when ethylene is the desired product, best results were obtained by operating a continuous recovery and recycling process in which the ethylene is extracted after each cycle and the residual heavier hydrocarbons (propane, propylene, and others) are mixed with the fresh charging stock.

Cambron and Bayley[56a] investigated the pyrolysis of ethane, propane and other hydrocarbons under conditions of streamline and turbulent flow in externally heated quartz tubes. With turbulent flow, higher rates of conversion to olefins were found.

The pyrolysis of liquid hydrocarbons and petroleum distillates to gaseous olefins has been the subject of a number of investigations. Although commercial cracking operations, particularly those at higher temperatures in the vapor phase, always yield considerable proportions of gaseous products containing as high as 50 per cent by volume of unsaturated hydrocarbons, their main object is to produce liquid hydrocarbons boiling in the gasoline range (i.e., up to about 200° C.). For this reason gas formation is generally minimized as far as possible. However, cracking as a means of producing gaseous olefins presents possibilities and might be economically feasible in countries where large supplies of such olefins are not otherwise available.

A study of the optimum conditions for producing gaseous olefins from a Pennsylvania straight-run gasoline (end point, 210° C.) by vapor phase pyrolysis at atmospheric pressure was made by Cassar.[57] The reaction vessel used by him consisted of a 3-foot length of 1-inch iron pipe packed with pumice and heated over a length of 30 inches. At a constant rate of feed, corresponding to a time of contact (of the liquid) of 5.66 hours, the total gas formation increased linearly with the temperature. The following empirical relation was found to exist:

$$G = 2.38\,(T - 480)$$

where G = volume of gas evolved per unit (liquid) volume of charge and T = temperature in °C. The proportion of olefins in the gas reached a maximum of 47 per cent by volume at about 600° C., and diminished at both higher and lower temperatures. At the above rate of feed, 135 volumes of gaseous olefins per unit (liquid) volume of feed were obtained at 600° C., corresponding to an optimum

[55a] *Ind. Eng. Chem.*, 1933, 25, 441.
[56] *Oil and Gas J.*, 1931, 29 (52), 22.
[56a] *Canadian J. Research*, 1933, 9, 175; *Chem. Abs.*, 1933, 27, 5172.
[57] *Ind. Eng. Chem.*, 1932, 24, 802.

concentration of olefins (45 per cent) in the gas. Maximum gas production, namely 650 volumes per unit (liquid) volume of feed, was obtained at 700° C. This gas, however, contained a lower proportion of olefins than that obtained at 600° C.

Cassar also determined the effect of varying the contact time on the yield of products at a constant temperature of 600° C. He found the relation between gas production and contact time to be

$$\log_e G = 0.0758\,\mathrm{H} + 5.18$$

in which G = volume of gas per unit (liquid) volume of feed, and H = time of contact (of liquid) in hours. This logarithmic relation indicates that the gas formed per unit of time is proportional to the quantity of gas already formed. This apparently means that a partly gasified (cracked) stock should gasify more readily than an uncracked stock.

It is interesting to note that the results of Gault and Hessel[88] on the cracking of hexadecane (in quartz tubes at various temperatures up to 815° C.) indicate that the volume of gaseous products formed at a constant rate of flow is directly proportional to the cracking temperature. A few experimental results of these investigators, showing the gas yields obtained under different conditions, are given in Table 33.

TABLE 33.—*Cracking of Hexadecane in Quartz Tubes.*

Temp. ° C.	Length of Furnace, Cm.	Rate of Feed, Cc. of Hexadecane per Minute	Liters of Gas per 100 Cc. Hexadecane	Unsaturated Hydrocarbons in Gas Per Cent
	Experiments at Constant Rate of Feed (1 cc. per min.)			
470°	64	1	0.18	28
540°	64	1	3.74	56
615°	64	1	13.60	47
685°	64	1	39.95	42
750°	64	1	46.60	35
815°	64	1	51.80	26
	Experiments at Varying Rates of Feed			
615°	32	0.33	17.75	56
615°	32	1	4.95	64
615°	32	2	2.70	73
685°	16	1	5.85	66
685°	32	2	5.70	68
685°	32	1	16.82	60
685°	48	1	25.70	51
685°	32	0.33	26.50	48
685°	64	1	39.95	42

Little information appears to be available with regard to the conditions necessary for the maximum yields of unsaturated gaseous hydrocarbons from the pyrolysis of petroleum distillates boiling above the gasoline range. Although the complete gasification of certain petroleum distillates to yield fuel gases (the so-called Blau gas and Pintsch gas being examples) has been practiced for many years, such processes are usually operated under conditions which permit the unsaturated hydrocarbon gases formed to undergo further changes. Optimum yields of unsaturated hydrocarbons are therefore not to be expected.

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[88] *Ann. chim.*, 1924, (10) 2, 209, 319; *Compt. rend.*, 1924, 179, 171; *Chem. Abs.*, 1925, 19, 966. See also Gault and Altchidjian, *Mat. grasses*, 1924, 16, 7006; 1925, 17, 7039; *Chem. Abs.*, 1925, 19, 1695; *J.S.C.I.*, 1925, 44, 61B; 1924, 43, 700B.

Some information on the gas yields obtained by the pyrolysis of a representative Mid-Continent gas oil in pyrex reaction tubes has been supplied by Geniesse and Reuter.[59] The results of some single-pass experiments at 640° to 700° C., in so far as they relate to gas production, are given in Table 34.

TABLE 34.—*Gas Production in the Cracking of Mid-Continent Gas Oil.*

				Composition of Gas, % by volume		
Temp. ° C.	Gaseous Contact Time, in Minutes *	Time-temperature Index	Gas Yields, % by Weight of Oil	Hydrogen	Ethylene	Total Unsaturated Hydrocarbons
625°	0.102	40	39.3	7.0	24	55
640°	0.013	8.6	11	5.1	27	57
640°	0.022	15	18	7.5	26	57
640°	0.051	35	29.3	6.0	25	59
640°	0.063	44	37.5	12.1	23	59
640°	0.081	56	43	7.1	24	58
640°	0.39	270	59(a)	7.9	20	50
660°	0.085	135	52.4	—	—	56
700°	0.023	185	65.5	8.5	28	58
700°	0.065	560	66.6(b)	9.9	25	54

* Times of contact calculated, assuming the gas laws, from the mean velocity of oil vapor entering tube and that of gases leaving furnace. (a) = 1.9% by weight of coke formed; (b) = 1.5% of coke.

The above results, all of which refer to a single treatment of the oil vapors in the cracking zone, show that the gas yields increase rapidly with rising temperature and attain a maximum of 65 to 66 per cent by weight at 700° C. The influence of the time-temperature index on the gas yields and the olefin content of the gases is shown graphically in Figure 15 in Chapter 3. If 480° C. is taken as a standard condition the time-temperature index of cracking may be calculated from the expression $2^{\frac{T-480}{17}}t$, in which T = cracking temperature in °C., and t = contact time in minutes.

Geniesse and Reuter also reported the results of a series of recycling experiments with a gas oil, from a Seminole crude, in which the products of pyrolysis were fractionated after each cycle and the fraction corresponding to the original gas oil (boiling point 225° to 260° C.) was subjected to further pyrolysis. Liquid fractions boiling below the gas oil range were counted as gasoline and higher-boiling residues were taken arbitrarily as tar. Residues remaining in the

TABLE 35.—*Recycling Experiments with Gas Oil.*

(Vapor-phase cracking at 600° C. and vapor contact time of 0.083 minute.)

Stage of Cracking	Original	1st Recycle	2d Recycle	3d Recycle	4th Recycle	5th Recycle
Yields:						
Gasoline, % by volume..	16.5	16.0	16.0	10.7	9.5	8.5
Gas, % by weight......	13.9	11.9	11.1	7.9	6.9	5.4
Tar, % by volume......	2.5	2.9	4.3	5.5	9.3	—
Coke, % by weight.....	0.054	0.097	0.12	0.19	0.17	0.26
Gas:						
Density	1.01	1.00	0.98	0.96	0.97	—
Hydrogen, % by volume.	8.0	—	9.4	—	—	19.7
Ethylene, % by volume..	24	—	22	—	—	17
Total unsaturated hydrocarbons, % by volume.	52	—	50	—	—	37

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[59] *Ind. Eng. Chem.*, 1930, 22, 1274.

cracking apparatus were designated as coke. Recycling was repeated until the quantity of gas oil remaining was too small for further experiments. Cracking conditions were maintained constant in each stage of pyrolysis at a temperature of 600° C. and a vapor-contact time of 0.083 minute. The results of these experiments are summarized in Table 35. All yields are expressed as percentages of the charge actually fed at each separate stage of cracking.

Contrary to the experience of Cassar[60] with gasoline, Geniesse and Reuter found that yields of gaseous products from partially cracked gas oil diminish on continued cycling. Furthermore, the hydrogen content of the gas increases, partly as a result of increased coke formation.

TECHNICAL PROCESSES

By subjecting the volatile products from the distillation of solid fuel, such as raw lignite, to the lowest temperature at which pyrolytic decomposition will occur, gaseous and liquid olefins are obtained without the formation of appreciable proportions of aromatics.[61] For example, the distillates from crude lignite when treated at 300° C. yield a gas containing 60 per cent carbon dioxide and 5 to 6 per cent olefins.

A method for obtaining gases rich in olefins by passing powdered or granular bituminous coal (either mechanically or by means of a carrier such as superheated steam) through a reaction zone heated to about 800° C. has been developed.[62] This process was extended later to include substances such as tar oils, mineral oils and their distillation residues, asphalts, or the residues obtained by the destructive hydrogenation of coal, tar, or mineral oils.[63] Granular materials, such as pumice, or slag, are impregnated with these substances and then treated at red heat in the same manner as pulverized coal. The rate of decomposition may be controlled by varying the size of the granules. Afterward the granules may be re-impregnated and used again. When necessary, the carbon deposited on them can be gasified in a producer.

In another process the raw materials (bituminous coal, tars, or mineral oils) are subjected to the action of an electrically heated zone in which granular conductive materials are kept in a state of agitation by gases or hydrocarbon vapors blown through them.[64] Carbonaceous or other non-conductive substances rendered conductive by impregnation with electrolytes may be employed. If the granular material is non-bituminous, the agitation must be accomplished with hydrocarbon vapors. The reaction products are gaseous and low-boiling olefins and diolefins.

Ethylene, propylene, butylene, and amylene may be manufactured by cracking mineral oils and tars at 600° to 800° C. in the presence of gases or vapors, such as water vapor.[65] Metals, alloys, or silicates, on which difficultly reducible oxides have been deposited, can be used as catalysts. The resulting gases contain 20 to 34 per cent of ethylene, 4 to 12 per cent of propylene and 1 to 5 per cent of butylene and amylene. Curme[66] suggested an alloy catalyst, predominantly of chromium and iron, for the thermal decomposition of hydrocarbons without the aid of steam.

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[60] *Loc. cit.*

[61] Chem. Fabr. Kalk G.m.b.H., German Patent 397,860, 1919; *J.S.C.I.*, 1924, **43**, 821B.

[62] I. G. Farbenindustrie A.-G., British Patent 301,775, 1927; *Brit. Chem. Abs.* **B**, 1929, 120. French Patent 643,413, 1929; *Chem. Abs.*, 1929, **23**, 1415. See also Davis, "Ethylene from Trent Amalgams as a Source of Alcohols," *Chem. Met. Eng.*, 1922, **27**, 1087.

[63] I. G. Farbenindustrie A.-G., British Patent 320,211, 1928; addition to British Patent 301,775, 1927; *Brit. Chem. Abs.* **B**, 1929, 1041.

[64] I. G. Farbenindustrie A.-G., British Patent 313,756, 1928; addition to British Patent 268,599, 1927; *Brit. Chem. Abs.* **B**, 1929, 634.

[65] I. G. Farbenindustrie A.-G., British Patent 315,895, 1928; *Brit. Chem. Abs.* **B**, 1929, 844.

[66] U. S. Patent 1,646,349, Oct. 18, 1927. Canadian Patent 268,569, 1927; *Chem. Abs.*, 1927, **21**, 2382.

Eldred and Mersereau[67] obtained gases rich in olefins by exposing the vapors of petroleum distillates (particularly the fraction boiling between 150° and 200° C.) for a short time to a temperature of about 700° C. and then quickly cooling. Davis and Murray[68] proposed subjecting the vapors of gas oil to a temperature of 600° to 650° C. In still another process mineral oils are conducted through a bath of fused material (e.g., lead) maintained at a temperature of 600° C. or higher. The products can be freed of undecomposed oil, gasoline, and diolefins by cooling and compression, or by absorption, and consist of methane, ethylene, propylene and butylene. The carbon, which separates, collects on the surface of the bath.[69]

Hydrocarbons containing more than four carbon atoms per molecule can be converted at 600° C. into a mixture of olefins and diolefins by passage over catalysts consisting of difficultly reducible oxides. Cyclohexane led over calcium aluminate at this temperature is converted principally into ethylene and butadiene.[70]

An apparatus has been proposed for the production of gaseous or very volatile olefins, in which the catalyst is kept at a constant temperature by being placed in thin layers on a good heat conductor through which a cooling fluid may be circulated.[71] The hot portions of the furnace are built of metals which do not promote carbon deposition (chromium, vanadium, manganese or steel alloys containing considerable proportions of the metals of the iron group, chromium, molybdenum, tungsten, vanadium, or manganese).[72] For example, V2A steel, or iron faced with a copper-manganese bronze and lined with calcium oxide and fragments of chromium, or iron coated with a thin layer of a paste made of potassium hydroxide, potassium silicate, kieselguhr and water and silicon carbide,[73] have been suggested. It has been pointed out by Häuber[74] that elemental silicon can be used for the conversion of low-boiling olefins to high-boiling olefins by heat.

Activated charcoal, made by passing steam over brown-coal coke at 800° to 900° C., has been suggested as a catalyst for the conversion of paraffins (especially those boiling below octane) into the corresponding olefins.[75] Other proposed catalysts are the metaphosphates of the metals in Group VI,[76] and oxides, such as calcium oxide, which are not easily reduced.[77]

Light hydrocarbons, such as propane or butane, are converted at comparatively low temperature into olefins when heated in the presence of halogens or halogen-containing substances.[78] Hydrogen chloride or organic halides may be used and, in addition, metals or metallic salts as activators. Thus, by using a few hundredths of one per cent by volume of iodine with propane at 575° C., unsaturated hydrocarbons, mainly ethylene, are formed to the extent of 15.5 per cent. At 650° C., 35.3 per cent of unsaturates is obtained. Butane in the presence of carbon tetrachloride at 600° C. yields butylene (6 per cent), propylene (14.3 per cent), and ethylene (21.9 per cent).

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[67] U. S. Patent 1,234,886, July 31, 1917; *Chem. Abs.*, 1917, **11**, 2609. The thermal decomposition of low-boiling petroleum fractions to yield propylene and butylene was noted as early as 1873 by Prunier (*Bull. soc. chim.*, 1873, (2) **19**, 109; *Chem. Soc. Abs.*, 1873, **26**, 487).

[68] British Patent 248,375, 1926; assigned to Petroleum Chemical Corp.; *Brit. Chem. Abs.* **B**, 1927, 403. See also Faber, *Western Gas*, 1932, **8**, 7, 39; *Chem. Abs.*, 1932, **26**, 5196.

[69] T. Goldschmidt A.-G., British Patent 232,568, 1925; *J.S.C.I.*, 1925, **44**, 949B.

[70] I. G. Farbenindustrie A.-G., British Patent 297,398, 1927; *Chem. Abs.*, 1929, **23**, 2722.

[71] I. G. Farbenindustrie A.-G., French Patent 660,560, 1928; *Chem. Abs.*, 1930, **24**, 127. *Cf.* British Patent 264,845, 1927; *Chem. Abs.*, 1928, **22**, 242.

[72] I. G. Farbenindustrie A.-G., British Patent 307,945, 1927; *Chem. Abs.*, 1930, **24**, 127. French Patent 653,646, 1928. *Cf.* British Patents 317,303 and 317,359, 1928; *Brit. Chem. Abs.* **B**, 1929, 886; also British Patent 297,398, 1927; *Chem. Abs.*, 1929, **23**, 2722.

[73] Imperial Chemical Industries, Ltd., French Patent 694,350, 1930: *Chem. Abs.*, 1931, **25**, 1838.

[74] German Patent 543,110, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2466. Also French Patent 717,056, 1931; *Chem. Abs.*, 1932, **26**, 2747. *Cf.* British Patent 339,274, 1929; *Chem. Abs.*, 1931, **25**, 2556; British Patent 336,234, 1929; *Chem. Abs.*, 1931, **25**, 1839.

[75] I. G. Farbenindustrie A.-G., British Patent 301,402, 1927; *Brit. Chem. Abs.* **B**, 1929, 122. British Patent 303,998, 1927; *Brit. Chem. Abs.* **B**, 1929, 235. See also Herrmann and Baum, Canadian Patent 279,622, 1928; *Chem. Abs.*, 1928, **22**, 2755. Krauch and Müller-Cunradi, U. S. Patent 1,881,692, Oct. 11, 1932; assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1933, **27**, 512.

[76] I. G. Farbenindustrie A.-G., British Patent 316,637, 1928; *Brit. Chem. Abs.* **B**, 1929, 843.

[77] Schmidt, Grosskinsky and Niemann, U. S. Patent 1,732,381, Oct. 22, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 127. *Cf.* British Patent 317,303, 1928; *Chem. Abs.*, 1930, **24**, 2139; French Patent 653,600, 1928; *Chem. Abs.*, 1929, **23**, 3715.

Van Peski[79] prepared unsaturated hydrocarbons by the decomposition of saturated hydrocarbons of higher molecular weight at comparatively low temperatures in the presence of sulphur, arsenic or antimony or mixtures of these elements and their compounds. Iodine or other halogens or halogen-containing compounds may be added if desired. For example, propane at 550° C., in the presence of tellurium on pumice and a small proportion of iodine, was found to yield a mixture of gases consisting largely of ethylene.

During the pyrolysis of paraffin hydrocarbons the olefins initially formed often undergo decomposition to yield methane. However, methane formation can be materially reduced by diluting the gaseous or vaporized hydrocarbons, prior to heating, with from 1 to 9 volumes of methane.[80] The process is best carried out at 600° to 700° C. and at atmospheric, somewhat reduced, or in some instances, elevated pressures. Catalysts include the oxides of zinc, magnesium, calcium, uranium, or silver on porous substances, pumice or artificial zeolite. Thus, mixtures of ethylene, propylene and isobutylene are obtained on passing mixtures of ethane, isobutane, methane and nitrogen at 650° C. through tubes of quartz or V2A steel containing pumice mixed with zinc oxide.

Wulff[81] proposed to manufacture gaseous unsaturated hydrocarbons, including acetylene, ethylene and allylene, by pyrolysis of paraffins (ethane, casinghead gasoline, gas oil or other petroleum fractions) at temperatures above 815° C. and under a partial pressure of 75 mm. or less. Low partial pressure is attained by mixing the vaporized raw material with a diluent such as steam, mercury vapor, or nitrogen. The duration of heating should be from 0.002 to 5 seconds, after which the reaction gases are immediately cooled. Reaction is carried out in non-ferrous refractory vessels, for example, carborundum tubes containing pieces of quartz, carborundum or sillimanite. Free oxygen should be excluded.

Baths of molten salts have been suggested as heating media for the cracking of hydrocarbons.[82] Thus, butane at 750° C. passed through an equimolecular mixture of barium and calcium chlorides (which melts at 500° C.) yields a product containing 18.5 per cent propylene and 18.7 per cent ethylene. Other salt mixtures, whose melting points range from 426° to 663° C., may be employed. Molten tellurium, in aluminum-lined steel vessels, is stated to catalyze such dehydrogenation reactions.

Catalysts consisting of the heavy metals of Groups I and VIII of the Periodic Table, e.g., copper, nickel, cobalt or platinum, have been recommended.[83] When such are used the temperature range for pyrolysis is 450° to 600° C., and the time of contact should be very short (less than 2 minutes). Other catalysts which have been proposed are fire-bricks impregnated with copper salts, or bricks made from fireclay and silicon or alloys of chromium or nickel, ferro-silicon, or silicon carbide[84]; zinc, chromium, molybdenum, tungsten[85] and titanium[85a]; elemental silicon or silicon deposited on a carrier[86]; elemental silicon mixed with a binder, clay or waterglass, or deposited on silica gel,[87] as well as elemental sulphur, antimony, arsenic, selenium and tellurium.[88] Among the various heating surfaces advocated, the following are said to minimize carbon deposition: unglazed porcelain impregnated with an oxide or oxides of chromium, tungsten, vanadium or uranium[89]; chromium, tungsten or molybdenum or alloys of these metals, or graphite[90]; elemental silicon[91]; refractory materials (chamotte or silicon carbide) covered with a glaze of a silicate, phosphate or borate of an alkali or alkaline earth metal, or of copper, manganese, lead or chromium[92]; iron alloys containing 10 to 16 per cent aluminum and as high as 6 per cent chromium (Ferralloy).[93]

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[78] Bataafsche Petroleum Maatschappij, British Patent 302,349, 1928; *Brit. Chem. Abs.* **B**, 1930, 406. Dutch Patent 23,704, 1931; *Chem. Abs.*, 1931, **25**, 3358.

[79] British Patent 315,890, 1928; *Chem. Abs.*, 1930, **24**, 1649.

[80] I. G. Farbenindustrie A.-G., British Patent 330,623, 1929; *Chem. Abs.*, 1930, **24**, 5764; also French Patent 684,854, 1929; *Chem. Abs.*, 1930, **24**, 5305.

[81] British Patent 334,178, 1929; *Chem. Abs.*, 1931, **25**, 962; *Brit. Chem. Abs.* **B**, 1930, 1056. See also Suida, Austrian Patent 127,401, 1931; *Chem. Abs.*, 1932, **26**, 3514.

[82] Bataafsche Petroleum Maatschappij, British Patent 334,241, 1929; *Chem. Abs.*, 1931, **25**, 1068. Dreyfus, British Patent 386,669, 1933; *Chem. Abs.*, 1933, **27**, 4388.

[83] Soc. des carburants synthétiques, British Patent 372,555, 1931; *Brit. Chem. Abs.* **B**, 1932, 714; French Patent 711,454, 1930, *Chem. Abs.*, 1932, **26**, 1615.

According to Binnie,[94] hydrogen chloride can be used as a diluent in the pyrolysis of methane and its homologues at temperatures of 1400° to 1450° C. The yield of acetylene is materially increased and the hydrogen chloride reacts but very little with the other gases present. It can be removed from the reaction products by washing with water.

Passing methane at high space velocities over a carbon catalyst at 700° to 1000° C. yields unsaturated hydrocarbons, particularly acetylene and ethylene.[95] A catalyst which is active in promoting this reaction is the lustrous graphite-like carbon deposit produced by the pyrolytic decomposition of hydrocarbons in the vapor phase in contact with lumps of clay or other refractory material. Not only methane but also its homologues may be used in producing unsaturated hydrocarbons, and dilution of the reacting gases with hydrogen is said to hinder the formation of carbon.

Wheeler, McAulay and Francis[96] proposed that in the decomposition of hydrocarbon vapors at 1000° to 1200° C. the reaction be effected in successive stages, each stage being at a higher temperature or at a lower space velocity than the preceding one. They also suggested that reaction tubes of bonded silicon carbide, bonded graphite mixture, or heat resisting alloy be used.

In the decomposition of hydrocarbons in successive stages,[97] the temperature can vary from 600° to 1000° C. in the different stages for gaseous mixtures containing very little methane, but for gases consisting mainly of methane temperatures higher than 1000° C. are necessary. As an alternative procedure the gaseous mixture is first separated into various fractions[98] and each fraction is subsequently submitted to pyrolysis under appropriate conditions of temperature.

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[84] I. G. Farbenindustrie A.-G., British Patent 337,434, 1929; *Chem. Abs.*, 1931, **25**, 2152; British Patent 364,106, 1930; *Chem. Abs.*, 1933, **27**, 1638; British Patent 366,102, 1930; *Chem. Abs.*, 1933, **27**, 2028.

[85] Frolich, U. S. Patent 1,869,681, Aug. 2, 1932; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1933, 536.

[85a] Gas Light and Coke Co., Ltd., British Patent 349.444, 1930; *Brit. Chem. Abs.* **B**, 1931, 794.

[86] I. G. Farbenindustrie A.-G., British Patent 339,274, 1929; *Chem. Abs.*, 1931, 25, 2556.

[87] I. G. Farbenindustrie A.-G., British Patent 357,170, 1930; *Chem. Age* (*London*), 1932, **26**, 128.

[88] Bataafsche Petroleum Maatschappij, Dutch Patent 23,704, 1931; *Chem. Abs.*, 1931, 25, 3358.

[89] I. G. Farbenindustrie A.-G., British Patent 366,107, 1930; *J. Inst. Pet. Tech.*, 1932, **18**, 120A. French Patent 717,412, 1931; *Chem. Abs.*, 1932, **26**, 2748.

[90] I. G. Farbenindustrie A.-G., British Patent 366,494, 1930; *J. Inst. Pet. Tech.*, 1932, **18**, 120A.

[91] I. G. Farbenindustrie A.-G., British Patent 368.291, 1930; *J. Inst. Pet. Tech.*, 1932, **18**, 161A. French Patent 717,494, 1931; *Chem. Abs.*, 1932, **26**, 2747.

[92] I. G. Farbenindustrie A.-G., British Patent 368,257, 1930; *Brit. Chem. Abs.* **B**, 1932, 458.

[93] Bampfylde, British Patent 364,043, 1931; assigned to British and Dominions Ferralloy, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 249.

[94] British Patent 343,881, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 433.

[95] Mittasch and Frankenburger, U. S. Patent 1.766.718, June 24, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 4305. *Cf.* British Patent 307,945, 1927; *Chem. Abs.*, 1930, **24**, 127.

[96] British Patents 342,319, 1929 and 342,359, 1930; both assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1931, 382. *Cf.* Imperial Industries, Ltd., French Patent 694,350, 1930; *Chem. Abs.*, 1931, **25**, 1838.

[97] British Patent 364,106, 1930; assigned to I. G. Farbenindustrie A.-G.; *J. Inst. Pet. Tech.*, 1932, **18**, 84A.

When inert hot gases are used as direct heating media for thermal decomposition of petroleum hydrocarbons they often become contaminated with hydrogen sulphide formed by the pyrolysis of the sulphur compounds present. Before such gases can be recycled they must be freed from hydrogen sulphide. Sachs[99] effected this by washing the cooled gases with water.

SEPARATION OF THE LOWER OLEFINS FROM GAS MIXTURES

The gases obtained by the pyrolysis of hydrocarbons usually consist of complex mixtures containing, in addition to the lower monolefins, hydrogen and paraffin hydrocarbons, some butadiene and a little acetylene. The extraction of individual olefins, or mixtures of them, from the complex gaseous mixture is a problem of great importance. Both physical and chemical methods are available for this purpose. The former include such well-known processes as fractional condensation or fractional distillation of the liquefied gas mixture as well as absorption by appropriate solvents and adsorption on solid materials. The chemical methods of separation make use of differences in the chemical reactivity of the various monolefins.

SEPARATION BY LIQUEFACTION AND RECTIFICATION

One of the most promising methods of separating the various constituents of a gas mixture is fractional condensation at successively lower temperatures or higher pressures, followed by fractional distillation (if necessary) of each fraction under appropriate conditions. Alternatively, the whole gas mixture can be liquefied and the liquefied gas subjected to fractional distillation. In general, fractional condensation will not effect complete separation. Better results are usually obtained by the careful distillation of the liquefied fractions.

Although the liquefaction of normally gaseous substances is facilitated by increased pressure, there exists a critical temperature for every gas, i.e., a temperature above which no amount of pressure alone will effect liquefaction. The pressure required to convert a gas to a liquid at the critical temperature is called the critical pressure. These fundamental constants[100] for various gaseous hydrocarbons present in cracking gas, together with their melting and boiling points, are as given in Table 36.

The wide differences between the critical temperatures of ethylene and propylene are noteworthy. Thus, gaseous propylene can be liquefied (under pressures up to 45 atmospheres) at all temperatures below 92.3° C., whereas ethylene is gaseous at all temperatures above 9.7° C. A partial separation of propylene from ethylene in mixtures of these gases is therefore possible by proper adjustment of the temperature and pressure. The separation, however, will not be complete because (1) at temperatures above 9.7° C. liquid propylene exerts a high vapor pressure and consequently will be present in considerable proportions with the ethylene in the gas phase, and (2) the liquefied propylene will contain appreciable quantities of dissolved ethylene. Accordingly, complete separation can be effected only by a fractional distillation of the liquefied propylene fraction.

The rapid advances in the technic of fractionation of very volatile hydro-

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[98] I. G. Farbenindustrie A.-G., British Patent 366,102, 1930; *J. Inst. Pet. Tech.*, 1932, 18, 126A.

[99] British Patent 336,380, 1929; assigned to Petroleum Conversion Corp.; *Brit. Chem. Abs.* B, 1931, 10.

[100] International Critical Tables, National Research Council, McGraw-Hill Book Co., Inc., New York, 1926.

TABLE 36.—*Constants for Various Gaseous Hydrocarbons Present in Cracking Gas.*

Gas	Melting Point, ° C.	Boiling Point, ° C.	Critical Temp., ° C.	Critical Pressure, Atmos.
Methane	−184°	−161.4°	−82.5°	45.8
Ethane	−172°	−88.3°	32.1°	48.8
Propane	−189.9°	−44.5°	95.6°	43
n-Butane	−135°	0.6°	153°	36
Isobutane	−145°	−10.2°	134°	37
Ethylene	−169.4°	−103.8°	9.7°	50.9
Propylene	−185.2°	−47.0°	92.3°	45
Acetylene	−81.8°	−83.6°[a]	36°	62
Allylene	−104.7°	−27.5°	128°	

[a] This is the sublimation point of acetylene at 760 mm. See McIntosh, *J. Phys. Chem.*, 1907, 11, 306; *Chem. Abs.*, 1907, 1, 1844.

carbons have been prompted largely by the development of the use of liquefied gases as fuel. This, in turn, is an outcome of efficient stabilization of volatile gasolines. The principal gaseous hydrocarbons involved in these commercial developments are propane and the butanes, but the same procedure with certain modifications can be applied to both higher and lower boiling hydrocarbons. Progress made in the practical rectification of such volatile hydrocarbons has been described by Carney.[101] He pointed out that olefins are usually separated from specially cracked material, the cracking process being such as to yield a product containing a large proportion of the desired olefin. Ethylene was the first olefin so manufactured and probably is still the one produced in the greatest quantity. Later propylene, butylenes, and amylenes, in varying degrees of purity, were separated from cracked gases and liquids. Such separations, of course, become more difficult as the molecular weight of the olefin, as well as the number of isomers, increase. Carney further reported that it is possible, for example, to separate 90 per cent butylene[101a] (a mixture of n- and iso-butylene) by fractionation of an iso- and n-butane fraction, or to vary the content of the more reactive butylene, isobutylene, from 5 per cent to more than 80 per cent in a fraction containing only hydrocarbons of four carbon atoms.

Fractionation methods under the proper operating conditions usually yield the olefin mixed with some of the corresponding paraffin. Separation of the olefin from its paraffin analogue can be accomplished by methods described below. For many purposes such separation is unnecessary and the paraffin-olefin mixture may be utilized directly for the preparation of various derivatives of its olefin constituent.

The process of Linde-Bronn, which has been applied in Germany and Belgium to the separation of the constituents of coke-oven gas, is of interest as illustrating the potentialities of low-temperature fractionation. It has been described by Bronn[102] and consists in cooling the coke-oven gas under pressure to separate first certain easily liquefiable impurities and later an ethylene-methane condensate. In this liquefaction step the coke-oven gas is cooled in a bath of liquid air or liquid nitrogen. Fractionation of the ethylene-methane condensate yields practically pure ethylene. Complete separation of methane and of carbon monoxide from the accompanying hydrogen can be accomplished by cooling the coke-oven gas, after removal of the ethylene-methane mixture, to a temperature of about —209° C. under 10 atmospheres pressure. This low temperature is secured with liquid nitrogen maintained under reduced pressure.

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[101] *J. Inst. Pet. Tech.*, 1932, 18, 701; for the rectification of propanes and butanes, see the following papers: Burket, *Nat. Pet. News*, 1931, 23 (11), 61; Kaye, *Petroleum Eng.*, 1931, 2 (6), 68; Smith, *Refiner*, 1931, 10 (6), 99.

[101a] See Bataafsche Petroleum Maatschappij, French Patent 740,837, 1932; *Chem. Abs.*, 1933, 27, 2741.

[102] U. S. Patent 1,211,395, Jan. 9, 1917; assigned to Rombacher Hüttenwerke; *J.S.C.I.*, 1917, 36, 205; German Patent 338,358, 1916; *J.S.C.I.*, 1921, 40, 684A; *Z. Kompr. Flüssige Gas*, 1926, 25, 5; *Jahrbuch Brennkrafttechnischen*, 1929, 9, 1.

Although most fractionations are carried out at constant pressure and at varying temperatures, a second method, namely, fractionation of the liquefied mixture at a constant temperature and gradually diminishing pressure, is also available. This process of "isothermal vaporization" has been used by Markovich and Pigulevski[103] for effecting a partial separation of the constituents of a liquefied cracking gas. This gas, produced in a semi-commercial vapor phase cracking unit operated at 580° to 620° C., was first liquefied at 100 atmospheres pressure at room temperature and then submitted to a slow, approximately isothermal vaporization. The analysis of this gas is given in Table 29 of Chapter 3.

Blanchet[104] devised a process for separating the constituents of cracking gas by fractional condensation. The crude gas from the cracking operation, whether oil-washed or not, is subjected to a temperature of about 5° C. under 2 to 5 atmospheres pressure. This removes any uncondensed pentanes and amylenes, which normally boil in the neighborhood of 35° C. The residual gases are further cooled to about 0° C. under 10 to 20 atmospheres. The butanes and butylenes are thus liquefied and withdrawn. The residual gas, containing ethylene, propylene, saturated hydrocarbons and hydrogen, is either subjected to a further cooling at higher pressures to effect liquefaction of the propylene, or is used directly for the preparation of mixtures of derivatives of ethylene and propylene.

According to Matthews and Bliss,[105] it is advantageous to fractionate unsaturated hydrocarbons in such a manner that all of the compounds in one fraction contain the same number of carbon atoms. The olefin in each fraction is then chlorinated to yield the corresponding dichloride.

By chilling cracking gas under a pressure of 100 to 120 pounds per square inch, Eldred and Mersereau[106] removed propylene and butylene as liquids, leaving ethylene and ethane in the gaseous condition. They stated, moreover, that ordinarily it is not practicable to condense ethylene and ethane by the application of high pressure and intense refrigeration, since ethylene is more easily separated in other ways, as for instance, by absorption.

Substantially pure propylene has been obtained from cracking gas in the following manner by Saunders.[107] The gas is first compressed under 100 atmospheres pressure to yield a liquid consisting of paraffins and higher olefins (butylene and amylene), together with some propylene and ethylene. By refrigerating and mixing the uncondensed gas with the liquid condensate under pressure, the propylene and ethylene present in the gas may be largely condensed to a liquid. The resulting liquid mixture is introduced under 15 to 20 atmospheres pressure into a fractionating column. The temperature of the lower end of this column is maintained at about 80° C. and that of the upper end at about 10° C. The gaseous products of this fractionation, containing a high percentage of both ethylene and propylene, are passed directly into a second similar column

[103] *Refiner*, 1932, **11**, 256, 303, 348. Also, *Neft. Khoz.*, 1929, **16**, 67; *Brit. Chem. Abs.* **B**, 1930, 130.

[104] British Patent 251,652, 1925; assigned to Soc. anon. d'explosifs et de produits chimiques; *Chem. Abs.*, 1927, **21**, 1546.

[105] U. S. Patent 1,158,524, Nov. 2, 1915; *Chem. Abs.*, 1916, **10**, 251; British Patent 15,048, 1913; *Chem. Abs.*, 1915, **9**, 127; *cf.* Matthews, Bliss and Elder, U. S. Patents 1,198,943 and 1,198,944, Sept. 19, 1916; *Chem. Abs.*, 1916, **10**, 3001; British Patent 17,234, 1912; *J.S.C.I.*, 1913, **32**, 884.

[106] U. S. Patent 1,234,886, July 31, 1917; assigned to Chemical Development Co.; *Chem. Abs.*, 1917, **11**, 2609.

[107] U. S. Patents 1,393,248 and 1.393,249, Oct. 11, 1921; assigned to Glysyn Corp.; *Chem. Abs.*, 1922, **16**, 489.

under the same pressure. The temperature limits in this latter step, however, vary from about 0° C. at the bottom to about —70° C. at the top of the column. Propylene separates in liquid form at the bottom of the apparatus. From the uncondensed gases passing off at the top, ethylene may be recovered by compression to 100 atmospheres and introducing the compressed gas into a third column maintained at a temperature of about —40° C. at the bottom and —65° C. at the top. Under these circumstances the ethylene separates (together with ethane) as a liquid at the bottom of this column.

As an alternative procedure, Saunders suggested distillation of the liquid condensate at somewhat higher pressures (25 to 35 atmospheres instead of 15 to 20) which condenses a larger proportion of liquid propylene at the bottom of the column. This liquid propylene can be further rectified by redistilling (under 25 to 35 atmospheres pressure) with a temperature gradient in the fractionating column from 0° C. at the bottom to 80° C. at the top. Almost pure gaseous propylene is obtained.

The many other possible combinations of temperature and pressure lead to a number of variations in this method of separation. Some advantage, however, is realized by using high pressures to reduce the amount of refrigeration otherwise required.

Pressure distillation at low temperatures has been applied in other instances to the separation of gaseous hydrocarbon mixtures. For example, a mixture of methane, ethylene and propylene is first liquefied and then subjected to a two-stage rectification process. Gaseous methane is taken off leaving a liquid ethylene-propylene fraction in the still, and this is subsequently distilled to yield ethylene (gaseous) and propylene (liquid). By using a compressed methane-ethylene mixture as an auxiliary heat-exchange material it is possible to apply the heat absorbed in cooling the fractionating columns to the distillation.[108] The separation of ethylene, propylene, and butadiene from cracking gas[109] is similarly accomplished.

Another system for the extraction of ethylene from gas mixtures consists in first liquefying a portion of the mixture and then scrubbing the gases with this liquid in countercurrent. The gases should be freed from such impurities as acetylene and the oxides of nitrogen before scrubbing. The scrubbing liquid rich in ethylene is later fractionated.[110]

The partial segregation of olefins in cracking gas has been described by Davis and Murray.[111] They proposed to separate the gaseous olefins into three main fractions corresponding to (1) an amylene fraction, (2) a butylene fraction, and (3) a mixture of ethylene and propylene. Saturated hydrocarbons are mixed with the olefins and some hydrogen as well with the ethylene-propylene fraction. To secure the partial separation the cracking gas is subjected to compression, distillation, condensation, and absorption in oil. As the various olefin fractions are employed primarily in the manufacture of secondary and tertiary alcohols this process is discussed in detail in Chapters 14 and 16.

The fractional distillation of mixtures of olefin and paraffin hydrocarbons in the presence of a selective solvent was suggested by Deanesly.[112] In the distillation of a liquefied mixture of butylenes and butane better separation between the saturated hydrocarbons and the olefins is secured by the use of such solvents as anhydrous ammonia or methylamine. Young and Perkins [112a] separate diolefins, olefins and paraffins by distillation in the presence of dioxane, nitrobenzene or dichloroethane.

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[108] Gesellschaft für Linde's Eismaschinen A.-G., British Patent 297,842, 1927; *Chem. Abs.*, 1929, **23**, 2771. French Patent 658,477, 1928; *Chem. Abs.*, 1929, **23**, 5066.

[109] I. G. Farbenindustrie A.-G., British Patent 302,203, 1927; *Brit. Chem. Abs.* **B**, 1929, 161.

[110] Société l'air liquide (Soc. anon. pour. l'étude et l'éxploitation des procédés Georges Claude); British Patent 308,687, 1929; *Brit. Chem. Abs.* **B**, 1930, 1055; French Patent 665,787, 1928; *Chem. Abs.*, 1930, **24**, 1393. German Patent 561,202, 1929; *Chem. Abs.*, 1933, **27**, 1065.

[111] British Patent 248,375, 1926; *Brit. Chem. Abs.* **B**, 1927, 403; U. S. Patent 1,790,517, Jan. 27, 1931; *Chem. Abs.*, 1931, **25**, 1374. Both patents assigned to Petroleum Chemical Corp.

[112] U. S. Patent 1,866,800, July 12, 1932; *Chem. Abs.*, 1932, **26**, 4611. U. S. Patent 1,893,733, Jan. 10, 1933; *Chem. Abs.*, 1933, **27**, 2158. Canadian Patent 312,393, 1931; *Chem. Abs.* 1931, **25**,

A combination of physical and chemical treatments is required in the exacting purification of ethylene used in anaesthesia.[113] Relatively warm ethylene is expanded from a pressure of about 100 atmospheres to condense out moisture and other impurities. The cold gas is then passed in heat-exchange relation with warm compressed ethylene and brought into contact with sulphuric acid of such concentration that higher olefins are absorbed without appreciable attack of the ethylene itself. The gas is neutralized with caustic potash solution, compressed, and dried, and again treated with sulphuric acid and neutralized. It is finally passed in heat-exchange relation with cold ethylene, and collected at a pressure less than that from which it was initially expanded.

SEPARATION OF OLEFINS BY THE USE OF ABSORBING LIQUIDS

A partial separation of the various lower olefins from one another, and from the corresponding paraffins, can be effected by taking advantage of the difference in their solubility in various liquid solvents. The dissolved gases can be liberated from solution by heating. Generally, the solubility of the olefins in neutral solvents increases with increasing molecular weight and, possibly on account of their greater reactivity, they are usually more soluble than the corresponding paraffins. Two types of solvents have been suggested: (1) certain organic solvents such as mineral oils or acetone in which the higher olefins are preferentially soluble, but which also tend to absorb relatively large proportions of the paraffins, and (2) certain solvents which dissolve the gaseous olefins by forming loosely bound addition compounds, but which do not dissolve saturated hydrocarbons. Solvents of this kind include aqueous solutions of metallic salts having an affinity for olefins, liquid sulphur dioxide and other similarly reactive solvents.

According to Podbielniak,[114] the extraction of ethylene from crude cracking gas can be accomplished by introducing the gas, under 400 to 500 pounds pressure, into a refrigerated fractionating column from which ethylene and some ethane are removed at the top, and propylene and heavier hydrocarbons at the bottom. Substantially pure ethylene may also be obtained by scrubbing the cracking gas with a solvent which absorbs ethylene, some of the heavier hydrocarbons and a small proportion of the methane. The ethylene and gaseous hydrocarbons are subsequently recovered from the enriched solvent by distillation. Almost pure ethylene is recovered from this distillate by pressure fractionation in a refrigerated column.

Curme [115] suggested countercurrent washing of gas mixtures, previously compressed so that the ethylene partial pressure amounts to several atmospheres, with an organic solvent such as acetone. The ethylene escapes from the wash liquid on releasing the pressure and may be further purified by distillation. If

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4011. Canadian Patent 314,643, 1931; *Chem. Abs.*, 1931, **25**, 5432. Patents assigned to Shell Development Co. Bataafsche Petroleum Maatschappij, British Patent 348,817, 1930; *Brit. Chem. Abs.* **B**, 1931, 709. French Patent 694,323, 1930; *Chem. Abs.*, 1931, **25**, 1839. German Patent 559,437, 1930; *Chem. Abs.*, 1933, **27**, 730.

[112a] Canadian Patent 328,052, 1932; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 991.

[113] Dawson, U. S. Patent 1,741,559, Dec. 31, 1929; assigned to Ohio Chemical and Manufacturing Co., *Brit. Chem. Abs.* **B**, 1930, 705; *Chem. Abs.*, 1930, **24**, 1124.

[114] *Oil and Gas J.*, 1931, **29** (52), 22.

[115] U. S. Patents 1,422,182, 1,422,183, and 1,422,184, July 11, 1922; *Chem. Abs.*, 1922, **16**, 3195 All patents assigned to Union Carbide Co.

propylene and other unsaturated hydrocarbons are present in the initial mixture they are dissolved and must be separated from the ethylene by a subsequent treatment. One process for accomplishing this consists in passing the gaseous mixture through absorption towers in contact with a cold petroleum oil, such as kerosene,[116] capable of absorbing propylene and the higher olefins without dissolving appreciable amounts of ethylene.

Ethyl alcohol [117] has also been used as a selective absorption solvent for olefins. Gases containing them are scrubbed under pressure with the alcohol, the solution passed into a flash tower and the olefin gases collected after scrubbing with water. The absorbing liquids may be distilled to recover the solvent.

Gas naphtha, a liquid recovered from the compression of cracked oil gas, has been suggested by Eldred [118] as an absorption medium since it dissolves propylene more readily than ethylene, which in turn is more easily absorbed than saturated hydrocarbons. Absorption of the gaseous olefins in this liquid is generally carried out under about 150 pounds pressure. Davis and Murray,[119] however, have shown that gas oil is a better solvent for the higher olefins, butylenes and amylenes, than for the lower ones, propylene and ethylene.

Aqueous solutions of silver, cuprous and mercury [120] salts are known to dissolve the gaseous olefins readily, probably by forming complex compounds. The olefins can be recovered from these solutions by warming or by reducing the pressure. There appear to be no published experimental data on the application of this method to the separation of individual olefins, although it is probable that all the olefins in a gaseous mixture are absorbed together. Horsley [121] recommended scrubbing coal gas with an acid solution of silver nitrate under ordinary or increased pressures at 0° to 10° C. to remove ethylene and other olefins, which may be recovered by heating the solution to 50° to 70° C., with or without reduction in pressure. An ammoniacal solution of a cuprous salt was suggested by Gordon and Hughes [122] for absorbing olefins (mainly ethylene) and carbon monoxide from coal gas, coke oven gas and similar gases under 150 to 250 atmospheres pressure. The gases released from the ammoniacal solution may be scrubbed with a solution of silver nitrate to absorb olefins and carbon monoxide. Anthes [123] proposed an ammoniacal solution of cuprous formate and separated any carbon monoxide simultaneously dissolved from the liberated olefins by preferential oxidation.

Plauson [124] has found that acetone will readily dissolve large volumes of sulphur dioxide and the resulting acetone-sulphur dioxide solution may be employed for the preferential solution of unsaturated hydrocarbons, particularly the diolefins.

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[116] Stewart, U. S. Patent 1,452,322, April 17, 1923; assigned to Dow Chemical Co.; *Chem. Abs.*, 1923, **17**, 1969. Horsley, British Patent 390,863, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1933, 661.

[117] Voorhees and Youtz, U. S. Patent 1,875,311, Aug. 30, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, **26**, 5962.

[118] U. S. Patent 1,465,600, Aug. 21, 1923; assigned to Carbide and Chemicals Corp.; *Chem. Abs.*, 1923, **17**, 3880.

[119] British Patent 248,375, 1926; *Brit. Chem. Abs.* **B**, 1927, 403. U. S. Patent 1,824,947, Sept. 29, 1931; *Chem. Abs.*, 1932, **26**, 291. Both patents assigned to Petroleum Chemical Corp.

[120] For example, Curme, U. S. Patent 1,315,541, Sept. 9, 1919; assigned to Union Carbide Corp.; *Chem. Abs.*, 1919, **13**, 2883.

[121] British Patent 291,186, 1927; assigned to Synthetic Ammonia and Nitrates, Ltd.; *Chem. Abs.*, 1929, **23**, 1136. Canadian Patent 284,405, 1928; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1929, **23**, 611. Imperial Chemical Industries, Ltd., French Patent 662,099, 1928; *Chem. Abs.*, 1930, **24**, 378. U. S. Patent 1,875,924, Sept. 6, 1932, assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, **27**, 101.

[122] British Patent 304,345, 1927; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 233. Also French Patent 662,099, 1928; *Chem. Abs.*, 1930, **24**, 378; see also Watts, British Patent 393,317, 1931, assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1933, 776. Imperial Chemical Industries, Ltd., French Patent 746,714, 1933; *Chem. Abs.*, 1933, **27**, 4546.

[123] German Patent 540,896, 1922; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2198.

[124] U. S. Patent 1,436,289, Nov. 21, 1922; *Chem. Abs.*, 1923, **17**, 627. See H. O. Traun's Forschungslaboratorium G.m.b.H., British Patent 156,123, 1920; *J.S.C.I.*, 1922, **41**, 403A.

For separating saturated and unsaturated liquid hydrocarbons, Johansen[125] utilized a dilute soap solution. Unsaturated hydrocarbons are more readily emulsified by such solutions and can be almost completely removed by careful adjustment of its concentration.

Ammonia has been suggested by Deanesly[125a] for the separation of butylene from butane.

SEPARATION OF OLEFINS BY ADSORPTION

Olefins can be preferentially adsorbed from gaseous mixtures of hydrocarbons on active charcoal,[126] silica gel, Florida or fuller's earth,[127] or other highly adsorptive materials, and subsequently recovered by heating the adsorbent, with or without the aid of superheated steam.[127a] The olefins appear to be much more readily adsorbed than the corresponding paraffins, and methane and hydrogen are adsorbed to only a small extent. Olefins of higher molecular weight are more easily adsorbed than ethylene, and hence this method allows ethylene to be separated from its homologues.[128] This method has been particularly recommended for the recovery of ethylene from mixtures, such as coal gas, containing relatively small initial concentrations.[129] In removing ethylene and methane from gaseous mixtures with activated charcoal at —60° C. (described by Behrens[130]) ethylene is adsorbed almost exclusively and may be recovered from the charcoal by heating to 150° to 225° C.

According to Harris,[131] the adsorbent used in separating individual olefins must first be saturated with a vapor or gas having an affinity for the adsorbent intermediate between those of the olefins to be adsorbed. For example, propylene may be separated from ethylene by passing the mixture over activated carbon saturated with water vapor.

Another process is the adsorption of olefins under pressure. Thus, the gases obtained by the treatment of hydrocarbons in the electric arc are conducted over charcoal under a pressure of 20 atmospheres to remove the acetylene.[132]

CHEMICAL SEPARATION OF OLEFINS

Perhaps the most obvious method for the separation of olefins from gaseous mixtures is absorption in a reagent capable of combining more readily with the olefins than with the other hydrocarbons present. Such methods include direct hydration, esterification with sulphuric acid or with the hydrogen halides, formation of chloro- and bromo-hydrins, direct halogenation,[133] and selective polymerization. These reactions are discussed in detail in other chapters[134] so that only very brief mention of some of them need be made here.

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[125] U. S. Patent 1,520,953, Dec. 30, 1924; assigned to Atlantic Refining Co.; *J.S.C.I.*, 1925, **44**, 163B.

[125a] British Patent 348,817, 1929; *Chem. Abs.*, 1932, **26**, 1939; German Patent 559,437, 1930; *Chem. Abs.*, 1933, **27**, 730; French Patent 694,323, 1930; *Chem. Abs.*, 1931, **25**, 1839; all patents assigned to Bataafsche Petroleum Maatschappij.

[126] Askenasy, U. S. Patent 1,865,422, July 5, 1932; assigned to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, **26**, 4347.

[127] Eisenhut and Schilling, U. S. Patent 1,894,763, Jan. 17, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2389. Seelig, German Patent 535,763, 1929; *Chem. Abs.*, 1932, **26**, 1113.

[127a] Wright (U. S. Patents 1,813,335 and 1,813,336, July 7, 1931; *Brit. Chem. Abs.* **B**, 1932, 405) suggested the use of allylenes or butylenes in conjunction with an adsorbent as a refrigerant.

[128] *Cf.* Gerr and Popov, *Neft. Khoz.*, 1926, **10**, 88; *Chem. Abs.*, 1927, **21**, 2788.

[129] See, for example, the following: Bronn, U. S. Patent 1,211,395, Jan. 9, 1917; assigned to Rombacher Hüttenwerke; *J.S.C.I.*, 1917, **36**, 205; British Patent 147,051, 1920, addition to 146,839; *J.S.C.I.*, 1922, **41**, 92A. Soddy, British Patent 125,253, 1918; *J.S.C.I.*, 1919, **38**, 352A. Bergius and Kalnin, British Patent 146,332, 1920; *J.S.C.I.*, 1921, **40**, 378A. Behrens, German Patent 370,037, 1921; assigned to Farbenfabrik vorm. F. Bayer and Co., *J.S.C.I.*, 1923, **42**, 593A. Connolly (U. S. Patent 1,909,811, May 16, 1933; assigned to Silica Gel Corp.; *Chem. Abs.*, 1933, **27**, 4069) extracts olefins from cracked distillate vapors by successive treatment with silica gel and sulphuric acid.

[130] German Patent 391,766, 1921; assigned to Farbenfabrik vorm F. Bayer and Co.; *J.S.C.I.*, 1924, **43**, 502B. See also Voronov, *Sintetichskii Kauchuk*, 1932, **1**, 7; *Chem. Abs.*, 1933, **27**, 1859.

[131] British Patent 331,787, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 978. U. S. Patent 1,872,080, Aug. 16, 1932; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1932, **26**, 6105.

[132] I. G. Farbenindustrie A.-G., British Patent 325,309, 1928; *Brit. Chem. Abs.* **B**, 1930, 406.

Direct esterification with hydrogen chloride, in both the liquid and gas phases, has been described. For example, a vapor phase cracking gas mixture containing 6 per cent butylenes, 17 per cent propylene, 27 per cent ethylene and 50 per cent methane is passed with the requisite amount of dry hydrogen chloride at 15° C. over a contact material consisting essentially of anhydrous ferric chloride.[135] On cooling to —60° C. butyl and propyl chlorides are condensed and the residual gas consists of 30 per cent ethylene and 70 per cent methane. Coffin, Sutherland and Maass[136] reported that the rates of reaction of anhydrous hydrogen chloride with the three butylenes differ so greatly that it is possible to use this reaction to separate the isomers. Thus, isobutylene is converted into the tertiary chloride at —78.5° C., but the other isomers are unaffected. Similarly, the work of Piotrowski and Winkler[137] indicates that, in the catalytic reaction of various amylenes with hydrogen chloride in the gas phase, low temperatures favor the formation of tertiary chlorides. Davis[138] suggested cold aqueous hydrochloric acid for the separation of liquid secondary and tertiary olefins. The latter react with the acid to give tertiary chlorohydrocarbons, which are removed from the unaffected secondary olefins by fractional distillation.

The numerous investigations of the reactions between sulphuric acid and olefins may be summarized briefly in the following manner. At ordinary temperatures, isobutylene and isoamylenes are absorbed in 60 per cent acid; the straight-chain amylenes and butylenes in 75 to 83 per cent acid; propylene, in acid of about 93 per cent concentration; and ethylene, only in 100 per cent acid at higher temperatures, 80° to 100° C.

A number of catalysts has been proposed for the separation of olefins by polymerization. Horsley[139] suggested conducting the gaseous mixtures containing olefins over a catalyst of acid cadmium phosphate at 150° to 200° C. under pressures greater than atmospheric. Under these conditions the homologues of ethylene undergo polymerization to condensable hydrocarbons but the ethylene passes on unchanged. According to Michel[140] when the gas mixture is led through a suspension of aluminum chloride in an inert solvent (e.g., decalin) at atmospheric or reduced pressures, the ethylene homologues are polymerized while ethylene escapes in a substantially pure condition.

PRODUCTION OF HIGHER OLEFINS BY PYROLYSIS

Liquid olefins occur in considerable quantities in commercial cracked gasolines. With the possible exception of the lower-boiling members, the pentenes and hexenes, their separation in a state even approaching purity is a matter of the greatest difficulty. The highest proportions of olefinic hydrocarbons are found in gasolines made by cracking heavier hydrocarbons in the vapor phase at atmospheric, or approximately atmospheric, pressure and at temperatures of the order of 600° C. The olefin content of cracked gasolines increases with rising cracking temperatures to a maximum and thereafter declines as a result of decomposition and polymerization. The application of pressure does not favor maximum production of olefins. In addition to acyclic olefins, cracked gasolines may contain appreciable amounts of diolefins and cyclic unsaturated hydrocarbons.

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[133] Prunier (*Bull. soc. chim.*, 1873, (2) **19**, 109; *Chem. Soc. Abs.*, 1873, **26**, 487) employed bromine for the separation of propylene and butylene, and Tinker (British Patent 108,602, 1916; *J.S.C.I.*, 1917, **36**, 998) used chlorine for the same purpose.

[134] See Chapters 6, 11, 12, 13, 15, and 26.

[135] T. Goldschmidt A.-G., British Patent 235,547, 1925; *J.S.C.I.*, 1925, **44**, 738B.

[136] *Canadian J. Research*, 1930, **2**, 267; *Chem. Abs.*, 1930, **24**, 3750.

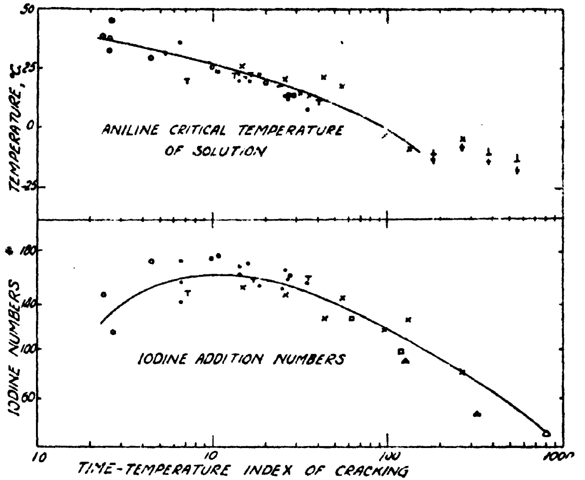
[137] *Przemysl Chem.*, 1931, **15**, 25; *Chem. Abs.*, 1931, **25**, 1794; *J. Inst. Pet. Tech.*, 1931, **17**, 225.

[138] U. S. Patent 1,790,519, Jan. 27, 1931; assigned to Petroleum Chemical Corp.; *Chem. Abs.*, 1931, **25**, 1374.

[139] British Patent 374,510, 1931; *Brit. Chem. Abs.* **B**, 1932, 832; U. S. Patent 1,893,586, Jan. 10, 1933; *Chem. Abs.*, 1933, **27**, 2285; both patents assigned to Imperial Chemical Industries, Ltd.

[140] U. S. Patent 1,822,358, Sept. 8, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 5901.

The influence of both time and temperature on the degree of unsaturation of the gasoline (end point, about 225° C.) made by cracking a Mid-Continent gas oil in the vapor phase in pyrex tubes has been investigated by Geniesse and Reuter,[141] who combined these two factors into a time-temperature index.[142] Their results, some of which are shown in Table 37, show that within the temperature range of 500° to 640° C., the iodine values of the cracked gasolines increase rapidly with rising time-temperature indices to a maximum of about 175 for a time-temperature index of about 10 and then gradually decrease (see Fig. 16).



Courtesy Industrial and Engineering Chemistry.

FIG. 16.—Relation between Time-Temperature Index of Cracking and Unsaturation. (Geniesse and Reuter.)

Higher olefins are obtained not only by thermal degradation of saturated hydrocarbons of higher molecular weight but also by polymerization of olefins of lower molecular weight. The thermal synthesis of higher olefins from lower members of the series is discussed more fully in Chapter 26. It may be noted, however, that in the controlled pyrolysis of the lower olefins not only higher olefins but also saturated acyclic and cyclic hydrocarbons are produced and it is difficult to stop polymerization at any desired stage. In relatively few instances only is it possible to effect the conversion of lower olefins into higher olefins without the simultaneous formation of comparatively large proportions of other hydrocarbons. Under carefully controlled conditions the partial conversion of ethylene into butylene appears possible, and Lenher[143] has found that the oxygen-

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[141] *Ind. Eng. Chem.*, 1930, 22, 1274.

[142] This expression is defined in a preceding section of this chapter.

[143] *J.A.C.S.*, 1931, 53, 2420, 3737, 3752. See also *J.A.C.S.*, 1932, 54, 1830 for the reaction between oxygen and propylene. This latter work is also discussed in Chapter 39.

TABLE 37.—*Cracking of Gas Oil in Pyrex Tubes.*

Temp. ° C.	Time of Contact, Minutes	Time-Temp. Index	Gasoline	
			Yield, % by Vol.	Iodine Values [a]
500°	1.1	2.42	13.0	148
500°	28.0	63	26.7	126
580°	0.047	2.7	9.7	117
580°	0.245	4.5	18.4	173
580°	0.168	9.8	24.1	174
580°	0.183	10.7	23.4	176
580°	0.473	27.5	26.2	161
600°	0.051	6.6	13.8	139
600°	0.107	14.1	20.7	168
600°	0.139	18.5	23.5	152
625°	0.02	7.2	15.1	147
625°	0.045	16.2	20	157

[a] Iodine values obtained by the method of Johansen, *Ind. Eng. Chem.*, 1922, 14, 288.

activated polymerization of ethylene can yield large amounts of propylene, besides other substances. The use of certain catalysts at comparatively low temperatures also renders possible the synthesis of higher olefins from lower members of the series.

PRODUCTION OF STYRENE AND ITS HOMOLOGUES BY PYROLYSIS

It has long been known that styrene is formed during the pyrolysis of coal and mineral oils. This hydrocarbon and its homologues have been found to be promising materials for the manufacture of other substances, particularly resins, to which they may be readily polymerized. The primary materials generally used in making styrenes by pyrolysis are ethylbenzene and its homologues. Thus, in the process described by Mark and Wulff,[144] benzene homologues containing at least one ethyl radical are catalytically dehydrogenated in the vapor phase at temperatures of 500° to 800° C. in the presence of an inert gaseous diluent such as steam, nitrogen, or carbon dioxide. Catalysts of the reaction include metallic compounds, particularly oxides and sulphides, which are nonreducible or only partially reducible under the working conditions, for example, the oxides of calcium, lithium, strontium, magnesium, beryllium, zirconium, tungsten, molybdenum or uranium; compounds such as chromium phosphate, calcium aluminate, magnesium chromate and calcium phosphate; anthracite, active carbon, silica gel, and clay; and mixtures of these substances with each other. The addition of 1 to 3 per cent of reducible metallic compounds, copper or iron oxides, frequently increases the catalytic activity. Pretreatment of the catalyst at 300° to 600° C. with gases free from carbon, such as hydrogen, steam, nitrogen or ammonia, is said to be advantageous in promoting its life and activity. This method of operation produces styrene from ethylbenzene and methylstyrene from ethyltoluene.

Smith[145] suggested the preparation of styrenes by heating an alkylbenzene and benzene to 600° to 750° C. in the presence of substances capable of forming stable compounds with the liberated hydrogen (sulphur or a mixture of sulphur and ethylene dichloride).

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[144] German Patent 550,055, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 4069. I. G. Farbenindustrie A.-G., British Patent 340,587, 1929; *Chem. Abs.*, 1931, 25, 4013. French Patent 702,377, 1930; *Chem. Abs.*, 1931, 25, 4285. *Cf.* British Patent 371,335, 1932; addition to British Patent 340,587; *Chem. Abs.*, 1933, 27, 3720. For the purification of styrene see Mark and Wulff, German Patent 534,476, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 738.

[145] British Patent 354,308, 1929; *Chem. Abs.*, 1932, 26, 5315; U. S. Patent 1,870,876, Aug. 9, 1932; *Chem. Abs.*, 1932, 26, 5580; both assigned to Naugatuck Chemical Co. Canadian Patent 308,122, 1931; assigned to Dominion Rubber Co., Ltd.; *Chem. Abs.*, 1931, 25, 1266. Also Naugatuck Chemical Co., French Patent 693,876, 1930; *Chem. Abs.*, 1931, 25, 1538.

Halogenated alkylbenzenes, such as chloroethylbenzene, may serve as the starting material. Thus, Smith and Jargstorff[146] made styrene by heating the halogenated hydrocarbon with a small quantity of the reaction product of pyridine, dibenzylamine, or aniline and hydrochloric, sulphuric or phosphoric acid. In other processes the halogenated alkylbenzene is heated in the presence of nonvolatile inorganic acids, such as sulphuric or phosphoric acid,[147] or in the presence of inorganic catalysts (mercurous, mercuric or zinc chlorides, mercuric oxide, sulphate or acetate).[148] As still another alternative, chloroethylbenzene is heated with an organic base (e.g., pyridine) to temperatures of 100° to 230° C. under pressures not exceeding 1 atmosphere.[149]

Aromatic hydrocarbons with unsaturated side chains may be prepared by the thermal dehydrogenation of the vapors of aromatic hydrocarbons having at least one saturated side chain of two or more carbon atoms at 450° to 700° C. under partial pressures less than atmospheric in the presence of such catalysts as oxides of cerium or zinc.[150] In this way styrene and vinylnaphthalene may be made from ethylbenzene and ethylnaphthalene, respectively.

Laage[150a] suggested the production of styrene by heating methylphenylcarbinol with a dehydrating catalyst.

ACETYLENE

Acetylene is one of the products of the pyrolysis of hydrocarbons at temperatures above 800° C. Below this temperature, however, it is formed in only small proportions. At the very high temperatures of the electric arc, high yields of acetylene are secured in the pyrolysis of all hydrocarbons.[151]

Acetylene is the only hydrocarbon known whose thermodynamic stability increases with rising temperature, but it is doubtful whether it ever becomes perfectly stable with respect to its elements. The boiling points of acetylene and some of its homologues are given in Table 38.

The occurrence of acetylene in the gases from high-temperature cracking (where temperatures range from 400° to 700° C.) has been recorded by several workers but the amounts actually present are, in all probability, very small. Though acetylene has been noted in small quantities among the products of the thermal decomposition of a number of hydrocarbons, particularly ethylene, ethane and paraffins of relatively low molecular weight, most of the work in this connection is concerned with the conversion of methane into acetylene. This interest in the formation of acetylene from methane is, no doubt, actuated by the fact that methane occurs in abundance in natural gas, coke-oven gas, and other gases, and its more efficient utilization is a problem of increasing importance.[152]

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[146] U. S. Patent 1,870,877, Aug. 9, 1932; assigned to Naugatuck Chemical Co. Canadian Patent 324,970, 1932; assigned to Dominion Rubber Co., Ltd.; *Chem. Abs.*, 1932, **26**, 5315. Also Naugatuck Chemical Co., French Patent 721,843, 1931; *Chem. Abs.*, 1932, **26**, 4069.

[147] Smith, U. S. Patent 1,870,878, Aug. 9, 1932; assigned to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, **26**, 5580.

[148] Jargstorff, U. S. Patent 1,870,852, Aug. 9, 1932; assigned to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, **26**, 5580.

[149] Naugatuck Chemical Co., British Patent 356,107, 1930; *Chem. Abs.*, 1932, **26**, 5579.

[150] I. G. Farbenindustrie A.-G., French Patent 721,597, 1931; *Chem. Abs.*, 1932, **26**, 4061. *Cf.* Suida, Austrian Patent 132,042, 1932; *Chem. Abs.*, 1933, **27**, 2691.

[150a] German Patent 533,827, 1925; *Chem. Abs.*, 1932, **26**, 737; French Patent 682,569, 1929; *Chem. Abs.*, 1930, **24**, 4523; both patents assigned to I. G. Farbenindustrie A.-G.

[151] The production of acetylene by the action of electrical energy on hydrocarbons is discussed more fully in Chapter 9. The industrial possibilities of acetylene production by pyrolysis of hydrocarbons are discussed by Storch (*Ind. Eng. Chem.*, 1934, **26**, 56).

[152] See *Chem. Met. Eng.*, 1931, **38**, 39.

TABLE 38.—*Acetylene and Its Homologues.*

		Boiling Point[a] °C.
Acetylene	$HC\equiv CH$	−83.6
Allylene	$HC\equiv CCH_3$	−27.5
Dimethylacetylene	$CH_3C\equiv CCH_3$	28.9
Ethylacetylene	$C_2H_5C\equiv CH$	18.5
Methylethylacetylene	$CH_3C\equiv CC_2H_5$	56
Propylacetylene	$C_3H_7C\equiv CH$	40
Isopropylacetylene	$(CH_3)_2CHC\equiv CH$	29.3
n-Butylacetylene	$C_4H_9C\equiv CH$	71.5
Methylpropylacetylene	$CH_3C\equiv CC_3H_7$	84

[a] International Critical Tables, National Research Council, McGraw-Hill Book Co., New York, 1926.

The work of Fischer[153] and Stanley and Nash[154] showed that acetylene is formed by the thermal decomposition of methane in the region of 1000° to 1200° C. provided the heating period is sufficiently brief. Ethylene, butadiene and aromatic hydrocarbons are obtained in addition to acetylene. In all probability, they state, the acetylene first formed is to be regarded as the intermediate in the synthesis of aromatic hydrocarbons.

Fischer and Pichler[155] studied the synthesis of acetylene from methane with reference to the equilibrium with benzene. At atmospheric pressure, time of contact 0.016 second and 1300° C., 60 grams of benzene and 75 grams of acetylene per cubic meter of methane were produced. Above 1400° C. only acetylene was obtained. A coke-oven gas, which contained 25 per cent methane, with time of contact 0.004 second at 1600° C. gave 75 per cent conversion of methane to acetylene. The yield of benzene from this gas was found to be small both at this and lower temperatures. Under reduced pressure (50 to 70 mm.) the yield of acetylene was 70 to 80 per cent, and that of the benzene fell as the pressure was reduced. The results conformed to the calculated equilibrium for the reaction $3C_2H_2 \rightleftarrows C_6H_6$.

When working at temperatures of 1600° to 2100° C. and using heating times varying from 0.03 to 75 seconds, Dubois[156] noted that methane yielded both acetylene and ethylene. The yield of acetylene, however, increased with increasing temperature and decreasing time of contact. Besides acetylene and ethylene, carbon black was obtained in considerable quantities. Under best conditions about 29 per cent of the methane was converted to unsaturated hydrocarbons, and the residual gas contained about 60 per cent hydrogen and 23 per cent methane.

The thermal decomposition of methane to acetylene was studied by Peters and Meyer.[157] By subjecting methane to temperatures of 1600° to 3000° C. in the presence of tungsten or carbon heating elements for extremely short intervals of time (as low as 0.0001 second) they secured excellent yields (as high as 65 per cent conversion) of acetylene, practically free from other hydrocarbons, except unchanged methane.[158]

The pyrolysis of methane in quartz tubes at temperatures of 1150° C. under pressures from atmospheric down to 25 mm. was investigated by Frolich, White and Dayton.[159] They too found it necessary to employ exceedingly short heating periods to avoid further decomposition of the acetylene initially formed. Heating for only 0.06 second at 1150° C. converted about 11 per cent of the methane to acetylene in the exit gas, and a reduction in pressure below atmospheric did not materially affect the conversion. When methane was cracked in an electric arc, acetylene was produced accompanied, however, by the deposition of large amounts of carbon. Dilution of the methane with hydrogen increased the yield of acetylene and reduced carbon formation. With methane and hydrogen in the ratio of approximately 1:2, as much as 51 per cent of the methane was converted to acetylene in one passage of the gas through the arc.[160] Biedermann and de Rudder[161] studied the pyrolysis of methane at 900° to 1500° C. and at pressures from 20 mm. to 760 mm. There was no appreciable decomposition below 1000° C., but ethylene formation was at a maximum at 1200° C. and 100 mm. Conversion to acetylene increased rapidly with rising temperature and at 1500° C. and 40 mm. the acetylene content of the reaction gas was 15 per cent (58 per cent of theoretical). Acetylene formation was always accompanied by the deposition of some carbon and it was also noted that hydrogen chloride, silica, thorium and nickel do not catalyze the decomposition of methane.

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[153] *Brennstoff-Chem.*, 1928, 9, 309; *Chem. Abs.*, 1929, 23, 2694. Also *Brennstoff-Chem.*, 1929, 10, 108; *Chem. Abs.*, 1929, 23, 4326.

[154] *J.S.C.I.*, 1929, 48, 1T.

[155] *Brennstoff-Chem.*, 1932, 13, 381; *Brit. Chem. Abs.* B, 1933, 10.

[156] *Gaz i Woda*, 1931, 11, 236, 270; *Chem. Abs.*, 1932, 26, 2577.

[157] *Brennstoff-Chem.*, 1929, 10, 324; *Chem. Abs.*, 1930, 24, 484. See also Peters, *Z. angew. Chem.*, 1930, 43, 855; *Chem. Abs.*, 1930, 24, 5715.

[158] The work of Peters and Fischer and their collaborators on the production of acetylene from methane at temperatures of the electric arc is discussed more fully in Chapter 9.

Dehydrogenation of ethylene to acetylene depends upon high temperature, a controlled brief time of heating, low pressure and dilution with hydrogen.[162] Without the addition of hydrogen and at atmospheric pressure, there was a maximum production (15 per cent) of acetylene at 1200° C. using a tube 3 mm. in diameter and rate of gas supply of 60 liters per hour; increasing the temperature caused separation of carbon. Dilution of the initial gas with hydrogen combined with a shorter time of heating decreased the formation of carbon and increased the yield of acetylene to 70 per cent. Oxygen added to the ethylene-hydrogen mixture did not improve the yield of acetylene. Ninety per cent conversion was effected when ethylene, either alone or diluted with hydrogen, was heated for very short periods of time to 1300° to 1400° C. under reduced pressure. At 1000° C. and 0.1 atmosphere, ethane was dehydrogenated to ethylene; at higher temperatures the main product was acetylene.

Fischer and Pichler[163] investigated the possibilities of using benzines and other petroleum distillates for the production of acetylene. They found that the yield of acetylene was very small when a benzine (boiling at 80° to 140° C.) was passed through a heated tube at 800° to 900° C. Larger yields were obtained at a lower pressure (about 0.1 atmosphere) and higher temperature. The deposition of carbon was reduced by dilution with hydrogen. At 1200° C., benzine diluted with hydrogen gave a 50 per cent yield of acetylene. The yield of acetylene was lower when a petroleum distillate (boiling from 180° to 250° C.) was thermally decomposed under similar conditions.

It is therefore evident that to produce good yields of acetylene from methane or other gaseous hydrocarbons it is necessary to apply as high temperatures as possible for very short periods. Somewhat reduced pressure and the addition of steam or hydrogen to the reacting gases tend to minimize decomposition of the hydrocarbons into carbon and hydrogen and thus assist in their conversion to acetylene.

[159] *Ind. Eng. Chem.*, 1930, **22**, 20.

[160] Frolich, White, Uhrmacher and Tufts, *Ind. Eng. Chem.*, 1930, **22**, 23.

[161] *Compt. rend.*, 1930, **190**, 1194; *Chem. Abs.*, 1930, **24**, 4255; *Bull. soc. chim.*, 1930, (4) **47**, 704.

[162] Fischer and Pichler, *Brennstoff-Chem.*, 1932, **13**, 406; *Brit. Chem. Abs.* **B**, 1933, 53.

[163] *Brennstoff-Chem.*, 1932, **13**, 441; *Brit. Chem. Abs.* **B**, 1933, 135.

Binnie and Wheeler[164] observed that the introduction of methane into the zone of reaction between hydrogen and chlorine made the energy of formation of hydrogen chloride available to energize the transformation of methane into acetylene. Under optimum conditions this permitted conversion of as much as 27 per cent of the methane into acetylene.

TECHNICAL METHODS FOR PRODUCING ACETYLENE

Knapp[165] described the preparation of acetylene from natural gas by passing the latter through a bed of incandescent carbon (air is excluded) maintained at a temperature higher than that attained by combustion. It is stated that a temperature of 2000° to 3500° C. is required and that the carbon reacts with the methane of the natural gas to yield acetylene:

$$CH_4 + 3C \longrightarrow 2C_2H_2.$$

Both ethylene and acetylene may be obtained by conducting methane under pressure at temperatures of 700° to 1000° C., or even higher, over a catalyst consisting of the alkaline-earth metal salts, silica, carbon, or the oxides of magnesium or beryllium, chromium, tungsten, vanadium or uranium,[166] or compounds of selenium, tellurium, or thallium.[167] Acetylene is the main product at high temperatures, if the gaseous products are quickly removed from the reaction zone. The production of acetylene by the pyrolysis of methane at 950° to 2000° C. and absolute or partial pressures of methane varying from 760 mm. at 950° to 25 mm. at 2000° C. has also been suggested.[167a]

An apparatus for effecting the cracking of methane to acetylene, or the pyrolysis of other hydrocarbon gases, has been described by Mittasch, Frankenburger and Wietzel.[168] The hydrocarbons are passed, alone or diluted with other gases, through a thin zone of high temperature which extends across substantially the whole cross-sectional area of a tube in the apparatus. A tungsten wire gauze carrying platinized asbestos in a thin layer or a highly porous refractory material such as "Marquardt composition" may be used as a catalyst.

Natural gas or gases produced during hydrogenation processes can be first converted by pyrolysis, at least partially, to liquid hydrocarbons, which are removed and the gaseous residue, either alone or mixed with other gaseous hydrocarbons, is cracked in an electric arc to yield acetylene.[169] Wulff[170] obtained acetylene by heating natural or manufactured gas to a temperature above 815° C. and quickly cooling the products of the reaction. To obtain the high temperatures necessary for the formation of acetylene from methane, Wulff[170a] burned an oxidizable gas within the interstices of a porous refractory material, which was subsequently heated electrically until the desired temperature was reached. The methane was then passed through the preheated porous material.

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[164] *J.S.C.I.*, 1931, **50**, 418T. Also, Wheeler and Binnie, British Patent 353,913, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1931, 959.

[165] U. S. Patent 1,023,783, April 16, 1912; assigned to United Gas Improvement Co.; *J.S.C.I.*, 1912, **31**, 481.

[166] I. G. Farbenindustrie A.-G., British Patent 366,107, 1930; *Brit. Chem. Abs.* **B**, 1932, 493.

[167] I. G. Farbenindustrie A.-G., British Patent 264,827, 1927; *Brit. Chem. Abs.* **B**, 1928, 327; *Chem. Abs.*, 1928, **22**, 242. Ruhrchemie A.-G., British Patent 391,206, 1931; *Brit. Chem. Abs.* **B**, 1933, 536. Frankenburger, German Patent 575,752, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4812. Fischer, German Patent 578,311, 1933; *Chem. Abs.*, 1933, **27**, 4239.

[167a] International Industrial and Chemical Co., British Patent 352,688, 1930; assigned to Soc. industrielle des hydrocarbures et dérivés; *Brit. Chem. Abs.* **B**, 1931, 959; also French Patents 692,451 and 692,452, 1929; *Chem. Abs.*, 1931, **25**, 1264.

[168] U. S. Patent 1,823,503, Sept. 15, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 150. I. G. Farbenindustrie A.-G., British Patent 264,845, 1926; *Chem. Abs.*, 1928, **22**, 242; French Patent 660,560, 1928; *Chem. Abs.*, 1930, **24**, 127. See also Herrmann and Baum, U. S. Patent 1,898,301, Feb. 21, 1933; assigned to Consortium für elektrochemische Industrie; *Chem. Abs.*, 1933, **27**, 2691.

[169] I. G. Farbenindustrie A.-G., French Patent 717,056, 1931; *Chem. Abs.*, 1932, **26**, 2747.

[170] U. S. Patent 1,843,965, Feb. 9, 1931; *Chem. Abs.*, 1932, **26**, 2040; Canadian Patent 306,263, 1930; *Chem. Abs.*, 1931, **25**, 715; British Patent 334,178, 1929; *Chem. Abs.*, 1931, **25**, 962. U. S. Patent 1,880,307, Oct. 4, 1932, *Brit. Chem. Abs.* **B**, 1933, 693. U. S. Patents 1,880,308, 1,880,309, and 1,880,310, Oct. 4, 1932; *Chem. Abs.*, 1933, **27**, 515.

Acetylene may be made by passing methane, preheated to 850° C., through a quartz tube in which a flame zone is fed by oxygen-delivery nozzles.[171] The temperature attained exceeds 1000° C. and the products are unaltered methane, acetylene, carbon monoxide and hydrogen. Acetylene is isolated by solution in acetone. In another method, also dependent upon incomplete combustion, methane is conducted through an iron tube lined with refractory material and oxygen is introduced through a series of nozzles so that a temperature of 1000° C. is reached. A variation is obtained by mixing combustible gases, methane, ethane, or hydrogen, with vaporized liquid hydrocarbons and rapidly heating the mixture to a high temperature by burning part of it with oxygen or gases containing oxygen.[172]

Winter, Hull and Ferguson[173] suggested the rapid passage of methane, mixed with oxygen or air, through a tube heated above 1000° C. The mixture should contain as much oxygen as possible, without becoming explosive, and pre-ignition may be prevented by placing a gauze before the reaction zone. By raising the temperature and selecting an optimum velocity, a maximum yield of about 10 per cent of acetylene is possible.

Wheeler and McAulay[174] have proposed heating unsaturated hydrocarbons to 1100° C. at a space velocity greater than 3000 reciprocal seconds. By heating ethylene, for example, to this temperature at a space velocity of 6400 reciprocal minutes, 30 per cent of the hydrocarbon is converted to a light oil and the reaction gas contains 8 per cent of acetylene.

Other methods involving heating periods of short duration have been described by Ferguson,[175] Voituron,[176] and Binnie.[177] Ferguson converted hydrocarbon gases or vapors, with the exception of methane, into acetylene by heating with a large excess of steam to temperatures above 1000° C. for not more than 2 seconds. The treatment of saturated hydrocarbons with steam and oxygen at temperatures around 1300° C. and at high space velocities was suggested by Voituron. On the other hand, Binnie used hydrogen chloride as a diluent and carried out the pyrolysis at temperatures of 1400° to 1450° C.

Banck[178] prepared acetylene by passing a preheated mixture of methane and an inert gas over an extensive surface of porous carbon electrically heated to 1400° to 2000° C. The pyrolysis of methane at temperatures of 950° to 2000° C. and at absolute or partial pressures of methane varying from 760 mm. at 950° C.

[170a] U. S. Patent 1,880.306, Oct. 4, 1932; *Chem. Abs.*, 1933, **27**, 544.

[171] I. G. Farbenindustrie A.-G., British Patent 265,234, 1926; *Chem. Abs.*, 1928, **22**, 243.

[172] I. G. Farbenindustrie A.-G., British Patent 290,322, 1927; *Chem. Abs.*, 1929, **23**, 846. See also Bataafsche Petroleum Maatschappij, British Patent 364,418, 1931; French Patent 713,012, 1930; *Chem. Abs.*, 1932, **26**, 1624. *Cf.* French Patent 725,114, 1931; *Chem. Abs.*, 1932, **26**, 4823. I. G. Farbenindustrie A.-G., British Patent 347,493, May 8, 1930; *Chem. Abs.*, 1932, **26**, 2752. Millar, U. S. Patent 1,896,552, Feb. 7, 1933; assigned to Shell Development Co.; *Chem. Abs.*, 1933, **27**, 2696. Haeuber and Linckh, U. S. Patent 1,894,765, Jan. 17, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2458.

[173] British Patent 332,731, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 893.

[174] British Patent 332,998, 1929; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 521.

[175] British Patent 342,771, 1929; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 5436. See also Ruhrchemie A.-G., British Patent 373,249, 1931; *Brit. Chem. Abs.* **B**, 1932, 832; French Patent 711,515, 1931; *Chem. Abs.*, 1932, **26**, 1938; British Patents 373,822 and 374,055, 1931; *Brit. Chem. Abs.* **B**, 1932, 832.

[176] British Patents 349,067 and 352,280, 1929; assigned to Soc. d'études scientifiques et d'entreprises industrielles; *Chem. Abs.*, 1932, **26**, 5315.

[177] British Patent 343,881, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**. 1931, 433.

[178] U. S. Patent 1,773,611, Aug. 16, 1930; *Brit. Chem. Abs.* **B**, 1931, 379.

down to 25 mm. at 2000° C. has also been suggested.[179] The ratio of surface to volume of the cracking chamber is increased at higher temperatures, being about 10:1 at 1500° C., and a halogen or halogen compound may be employed as a catalyst.

Two-stage processes for the conversion of aliphatic into aromatic hydrocarbons, in which acetylene is formed in the first stage, have also been advocated. Thus, aliphatic hydrocarbons are heated to temperatures exceeding 1600° C. for less than 0.001 second[180] or to temperatures above 1120° C. under reduced pressure for less than 0.5 second[181] to yield gas mixtures containing acetylene. The mixtures are further heat-treated in a second stage of the process to form aromatic hydrocarbons.[182]

SEPARATION OF ACETYLENE

For separating acetylene from the gaseous products of pyrolytic reactions advantage is generally taken of the solubility of this compound in various solvents. The gas is washed either with water,[182a] or better with acetone,[183] under slightly increased pressure when solution of the acetylene in the solvent readily takes place. Various other organic solvents, suggested by Horsley and Roffey,[184] are ethers or esters boiling above 100° C., especially the esters, ethers, or ester-ethers of polyhydric alcohols. Those suggested are: glycol monoformate, mono- and di-alkyl ethers of ethylene glycol, glycerol mono- and di-acetates, glycerol mono-, di-, and tri-alkyl ethers, esters of mono- and di-alkyl ethers of glycerol, esters of phthalic acid, and ethyl lactate.

Acetylene may be washed out of gas mixtures by low-boiling liquids of the nature of the commonly used refrigerants, e.g., liquid sulphur dioxide, carbon dioxide, anhydrous ammonia, methyl chloride, and ethyl chloride.[185] Metzger suggested the separation of acetylene from other hydrocarbons by bringing the mixed gases into contact with ethyl carbonate which is said to selectively absorb acetylene.[186] Nicodemus[186a] suggested acetonitrile at —10° C. as a selective solvent for extracting acetylene from gas mixtures.

Gaseous mixtures produced by the action of the electric arc on hydrocarbons contain not only acetylene but also highly unsaturated gaseous hydrocarbons such as diacetylene, allylene and butadiene. These latter may be removed by passing the gas over heated silica gel[187] or kieselguhr, by washing with nitrobenzene, gas oil of density 0.88 or halogenated hydrocarbons,[188] or by bringing them into contact with agents such as sulphuric or phosphoric acids,[189] which polymerize the highly unsaturated hydrocarbons. Wright[190] suggested allylene and 2-butene adsorbed on silica gel for use in refrigerating systems.

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[179] International Industrial and Chemical Co., Ltd., British Patent 352,688, 1930; assigned to Soc. industr. des hydrocarbures et dérivés; *Brit. Chem. Abs.* **B**, 1931, 959. Also French Patents 692,541 and 692,542, 1929; *Chem. Abs.*, 1931, **25**, 1264.

[180] Ruhrchemie A.-G., British Patent 373,249, 1931; French Patent 711,515, 1931; *Chem. Abs.*, 1932, **26**, 1938.

[181] Ruhrchemie A.-G., British Patents 373,822 and 374,055, 1931; additions to British Patent 373,249, 1931; *Brit. Chem. Abs.* **B**, 1932, 832.

[182] See Chapter 5 for details of the production of aromatic hydrocarbons.

[182a] I. G. Farbenindustrie A.-G., British Patent 280,885, 1927; *Brit. Chem. Abs.* **B**, 1928, 778.

[183] Ruhrchemie A.-G., French Patent 748,193, 1933; *Chem. Abs.*, 1933, **27**, 5175.

[184] British Patent 331,654, 1929; *Chem. Abs.*, 1931, **25**, 116; U. S. Patent 1,854,141, April 12, 1932; *Chem. Abs.*, 1932, **26**, 3364. Both patents assigned to Imperial Chemical Industries, Ltd.

[185] I. G. Farbenindustrie A.-G., British Patent 377,193, 1931; *Brit. Chem. Abs.* **B**, 1932, 926. French Patent 724,476, 1931; *Chem. Abs.*, 1932, **26**, 4823.

[186] U. S. Patent 1,900,655, Mar. 7, 1933; assigned to Air Reduction Co.; *Chem. Abs.*, 1933, **27**, 2966.

[186a] U. S. Patent 1,813,946, July 14, 1931; *Chem. Abs.*, 1931, **25**, 5277; British Patent 303,068, 1928; *Brit. Chem. Abs.* **B**, 1929, 547; both patents assigned to I. G. Farbenindustrie A.-G.

[187] I. G. Farbenindustrie A.-G., French Patent 716,882, 1931; *Chem. Abs.*, 1932, **26**, 2202.

[188] I. G. Farbenindustrie A.-G., British Patent 386,052, 1931; *Brit. Chem. Abs.* **B**, 1933, 216; French Patent 739,289, 1932; *Chem. Abs.*, 1933, **27**, 1896; Baumann, Bückert, Sandhaas, and Schilling, German Patent 578,072, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4252. Standard Oil Development Co., French Patent 744,772, 1933; *Chem. Abs.*, 1933, **27**, 4252.

Askenasy[191] used an adsorbent, such as activated charcoal, for separating acetylene from gas mixtures containing ethylene, methane, hydrogen, some nitrogen and a little acetylene. The gas is passed through the adsorbent which is afterward subjected to evacuation without heating. This releases chiefly methane and hydrogen, the acetylene being recovered by heating and further evacuation.

Acetylene may be separated from diacetylene, allylene, allene or butadiene by freezing the latter hydrocarbons out of the mixture at temperatures of —30° to —81° C.[192] To facilitate its transportation and storage, the conversion of acetylene to a solid by pressure has been proposed.[193]

DIOLEFINS

The diolefins are hydrocarbons possessing two double bonds and are typified by the examples in the aliphatic series given in Table 39.

Table 39.—*Typical Diolefins of the Aliphatic Series*

		Boiling Point[a] °C.
Propadiene (Allene)	$CH_2{=}C{=}CH_2$	—32
1,2-Butadiene (Methylallene)	$CH_2{=}C{=}CHCH_3$	19
1,3-Butadiene (Divinyl)	$CH_2{=}CHCH{=}CH_2$	—2.6
2,3-Pentadiene (sym.-Dimethylallene)	$CH_3CH{=}C{=}CHCH_3$	51
2-Methyl-1,2-butadiene (unsym. Dimethylallene)	$(CH_3)_2C{=}C{=}CH_2$	40.5
2-Methyl-1,3-butadiene (Isoprene)	$CH_2{=}C(CH_3)CH{=}CH$	34
1,3-Pentadiene (Piperylene)	$CH_3CH{=}CHCH{=}CH$	44
2,3-Dimethylbutadiene (Diisopropenyl)	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	69.6
1,5-Hexadiene (Diallyl)	$CH_2{=}CHCH_2CH_2CH{=}CH_2$	60
2,4-Hexadiene (Dipropenyl)	$CH_3CH{=}CHCH{=}CHCH_3$	82

[a] International Critical Tables, McGraw-Hill Book Co., New York, 1926.

Many carbocyclic diolefins, including a large number with a conjugated system of double bonds, are known. Little has been recorded about the occurrence of these cyclic diolefins in the products of the pyrolysis of hydrocarbons but several, particularly cyclopentadiene, have been identified in low-boiling fractions from the high-temperature carbonization of coal.

From the point of view of the organic chemist, the most interesting members of the series are those possessing a conjugated system of double bonds, such as butadiene (1,3-butadiene is usually called simply butadiene) and isoprene. This type of unsaturated linkage appears to be connected with the remarkable properties of these compounds, whose tendency to polymerize to substances of high molecular weight among which are the so-called synthetic rubbers, calls for special attention.

Although there is very little evidence of the presence of allene in the gaseous products of the cracking of hydrocarbons, considerable data are available on the occurrence of butadiene, the other diolefin which is gaseous at ordinary temperatures, among the products of thermal decomposition of all kinds of hydrocarbons and of petroleum distillates. In fact, butadiene is probably an important intermediate in the formation of cyclic, particularly aromatic, hydrocarbons in thermal processes. It occurs to the extent of about 2 per cent in the gases from commercial vapor phase cracking operations, but apparently it is formed to only a trifling extent during liquid phase cracking at lower temperatures.

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[189] I. G. Farbenindustrie A.-G., British Patent 368,782, 1930; *Brit. Chem. Abs.* **B**, 1932, 491. Auerhahn, German Patent 568,630, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2638.

[190] U. S. Patents 1,813,335 and 1,813,336, July 7, 1931; *Chem. Abs.*, 1931, **25**, 5224.

[191] U. S. Patent 1,865,422, July 5, 1932; *Chem. Abs.*, 1932, **26**, 4347. German Patent 556,776, 1928; *Chem. Abs.*, 1933, **27**, 312; French Patent 678,830, 1929; *Chem. Abs.*, 1930, **24**, 3519; all patents assigned to Soc. anon. pour l'ind. chim. à Bâle; *cf.* I. G. Farbenindustrie A.-G., French Patent 688,186, 1930; *Chem. Abs.*, 1931, **25**, 752; French Patent 716,882, 1931; *Chem. Abs.*, 1932, **26**, 2202.

[192] I. G. Farbenindustrie A.-G., British Patent 371,142, 1931; *Brit. Chem. Abs.* **B**, 1932, 762.

[193] I. G. Farbenindustrie A.-G., British Patent 351,634, 1930; *Chem. Abs.*, 1932, **26**, 4447.

Of the higher aliphatic dienes, isoprene is of most interest since it was the raw material for the first synthetic rubber-like substances. Its existence in the products of pyrolysis of hydrocarbons has been definitely shown, but the quantities of it available are certainly much smaller than of butadiene. The probable presence of another butadiene homologue, namely 1,3-pentadiene (piperylene) in a sample of cracked spirit from the Cross process was indicated by the work of Brame and Hunter.[194]

ISOPRENE

Williams[195] appears to have been the first to prepare isoprene by the dry distillation of rubber. Later, Ipatiev and von Wittorf[196] observed that trimethylethylene was also formed by this method. Hlasivetz and Hinterberger[197] and Tilden[198] produced isoprene by passing turpentine through red-hot iron tubes. Mokievski[199] found that the products of this treatment (amounting to 1.5 to 3 per cent of the turpentine) contained 50 per cent isoprene and that the remainder consisted, for the most part, of trimethylethylene. Later workers reported various yields. Harries and Neresheimer[200] obtained about 10 per cent of isoprene by decomposing turpentine, dipentene or limonene over a glowing platinum spiral. They also prepared this diolefin by the action of soda-lime on a dihalogen compound of isopentane. According to Staudinger and Klever,[201] yields as high as 60 per cent of isoprene may be secured by decomposing limonene at low pressures (4 mm.) by means of an electrically heated platinum spiral. Others have indicated that the optimum temperature for the production of isoprene by the pyrolysis of turpentine, pinene or limonene or similar materials in the presence of glass, porcelain or other contact materials lies between 450° and 700° C.[202]

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[194] *J. Inst. Pet. Tech.*, 1927, **13**, 794; *Chem. Abs.*, 1928, **22**, 2832. *Cf.* Armstrong and Miller, *J.C.S.*, 1886, **49**, 83.

[195] *Proc. Roy. Soc.*, 1860, **10**, 516; *Jahresberichte*, 1860, 495; Gmelin-Watts, Handbook of Chemistry, Cavendish Society, London, 1862, **14**, 331. *Cf.* also, Bouchardat, *Bull. soc. chim.*, 1875, (2) **24**, 108; *Compt. rend.*, 1875, **80**, 1446; *Chem. Soc. Abs.*, 1875, **28**, 1259. Wallach, *Ann.* 1885, **227**, 295; *Chem. Soc. Abs.*, 1885, **48**, 550.

[196] *J. prakt. Chem.*, 1897, (2) **55**, 1; *Chem. Soc. Abs.*, 1897, **72** (1), 233.

[197] *Z. für Chem.*, 1868, (2) **24**, 380. *Cf.* Hlasivetz, *Ber.*, 1876, **9**, 1991.

[198] *Jahresberichte*, 1882, 406; *Chem. News*, 1882, **46**, 120; *Chem. Soc. Abs.*, 1883, **44**, 75. *J.C.S.*, 1884, **45**, 410.

[199] *Chem. Ztg.*, 1895, **19**, 2254; *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 885; *Chem. Zentr.*, 1899, **1**, 589; *Chem. Soc. Abs.*, 1899, **76** (1), 726.

[200] *Ann.*, 1911, **383**, 157; *Chem., Soc. Abs.*, 1911, **100** (1), 798. See also Harries and Gottlöb, *Ann.*, 1911, **383**, 228; *Chem. Soc. Abs.*, 1911, **100** (1), 798; Harries, German Patents 243,075 and 243,076, 1910; *J.S.C.I.*, 1912, **31**, 302; U. S. Patent 1,038,359, Sept. 10, 1912; assigned to Farbenfabr. vorm. F. Bayer and Co., *J.S.C.I.*, 1912, **31**, 951. Gottlöb, British Patent 18,431, 1911; *Chem. Abs.*, 1913, **7**, 426; U. S. Patent 1,065,522, June 24, 1913; *Chem. Abs.*, 1913, **7**, 2863; German Patent 269,240, 1912; *Chem. Abs.*, 1914, **8**, 2073.

[201] *Ber.*, 1911, **44**, 2212, Staudinger, U. S. Patent 1,065,182, June 17, 1913; *Chem. Abs.*, 1913, **7**, 2693.

[202] Woltereck, British Patent 27,908, 1909; *Chem. Abs.*, 1911, **5**, 2979. Heinemann, British Patent 14,040, 1910; *Chem. Abs.*, 1911, **5**, 3347. British Patent 1,953, 1912; *Chem. Abs.*, 1913, **7**, 2487. U. S. Patent 1,092,838, April 14, 1914; *Chem. Abs.*, 1914, **8**, 2072. German Patent 278,104, 1914; *Chem. Abs.*, 1915, **9**, 1136. U. S. Patent 1,095,395, May 5, 1914; *Chem. Abs.*, 1914, **8**, 2268. U. S. Patent 1,159,380, Nov. 9, 1915; *Chem. Abs.*, 1916, **10**, 295.

Hofmann and Tank, U. S. Patent 1,010,050, Nov. 18, 1911; *Chem. Abs.*, 1912, **6**, 431.

Silberrad, British Patent 4,001, 1910; *Chem. Abs.*, 1911, **5**, 3124. U. S. Patent 1,022,338, April 2, 1911; *Chem. Abs.*, 1912, **6**, 1686. German Patent 240,074, 1910; *Chem. Abs.*, 1912, **6**, 2186.

Stephan, U. S. Patent 1,057,680, April 1, 1913; *Chem. Abs.*, 1913, **7**, 1814. Webel, U. S. Patents 1,083,164 and 1,083,165, Dec. 30, 1913; *Chem. Abs.*, 1914, **8**, 830.

According to Graul, Hanschke and Webel [203] isoprene may be prepared from isopentane obtained from petroleum or oil gas. Isopentane is chlorinated and the chloro-isopentanes are treated with lime to remove hydrogen chloride and form trimethylethylene. This substance is then converted, by the addition of halogens, into a dihalide from which hydrogen halide is again removed. In this manner substantially pure isoprene is produced.

BUTADIENE

The 1,3-butadiene has been known for many years under a number of names, such as bi- or di-vinyl, diethenyl, erythrene, pyrolylene, and vinylethylene. By the term *butadiene* is generally meant the 1,3-isomer, rather than the 1,2-isomer, as it has been studied more extensively. Berthelot [204] obtained butadiene by passing a mixture of acetylene and ethylene through a red-hot porcelain tube. It was found in illuminating gas by Caventou [205] and by Armstrong and Miller.[206] It is formed when ethylene,[207] isobutylene,[208] pentane and hexane [209] are conducted through heated tubes. The decomposition of alcohol vapors in the presence of aluminum [210] and the pyrolysis of fusel oil [211] also yield this hydrocarbon.

The almost universal appearance of butadiene in the gaseous products of pyrolysis of all types of hydrocarbon materials, at temperatures immediately below those at which aromatic hydrocarbon formation becomes marked, led to the conviction that butadiene is an important intermediate in the transformation of straight-chain hydrocarbons into aromatics.[212] The evidence for this view is largely indirect. For example, Zanetti, Suydam, and Offner [213] found that the optimum temperature for the production of butadiene (750° C.) in the pyrolysis of ethylene was coincident with the initial appearance of aromatic substances in the products. Later, however, Wheeler and Wood [214] demonstrated that butadiene condenses with olefins at cracking temperatures to yield cyclohexene and its homologues, which rapidly lose hydrogen and are converted into aromatics. The production of hydroaromatics (and from them, of aromatics) is

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Ostromislensky, U. S. Patent 1,108,781, Aug. 25, 1914; *Chem. Abs.*, 1914, **8**, 3506. Dutch Patent 291, 1914; *Chem. Abs.*, 1914, **8**, 3245; Swedish Patent 37,268, 1912; *Chem. Abs.*, 1915, **9**, 2328. French Patent 442,980, 1912; *Chem. Abs.*, 1913, **7**, 1815. British Patent 6,301, 1912; *Chem. Abs.*, 1913, **7**, 3038. German Patent 266,402, 1912; *Chem. Abs.*, 1914, **8**, 832.

Gross, U. S. Patent 1,099,498, June 9, 1914; *Chem. Abs.*, 1914, **8**, 2816. British Patent 13,825, 1913; *Chem. Abs.*, 1914, **8**, 3867.

Nauck, German Patent 264,902, 1912; *Chem. Abs.*, 1914, **8**, 267.

Kyriakides and Earle, U. S. Patents 1,094,222 and 1,094,223, April 21, 1914; *Chem. Abs.*, 1914, **8**, 2072. U. S. Patent 1,106,290, Aug. 4, 1914; *Chem. Abs.*, 1914, **8**, 3245.

Badische Anilin- and Soda-Fabrik, British Patent 975, 1913; *Chem. Abs.*, 1914, **8**, 2497.

von Euler-Chelpin, Swedish Patent 36,863, 1912; *Chem. Abs.*, 1915, **9**, 2328.

Holt, U. S. Patent 1,168,070, Jan. 11, 1916; *Chem. Abs.*, 1916, **10**, 986; Chem. Fabrik auf Aktien v. E. Schering, French Patent 438,789, 1912; *Chem. Abs.*, 1912, **6**, 3200. German Patent 260,934, 1911; *Chem. Abs.*, 1913, **7**, 3425.

Callender, British Patent 17,397, 1912; *Chem. Abs.*, 1914, **8**, 433.

[203] U. S. Patent 1,298,929, April 1, 1919; assigned to Alien Property Custodian; *Chem. Abs.*, 1919, **13**, 1954. Badische Anilin- and Soda-Fabrik, French Patent 435,312, 1911; *J.S.C.I.*, 1912, **31**, 409; Dutch Patent 2,051, 1917; *Chem. Abs.*, 1917, **11**, 3470.

[204] *Ann. chim.*, 1866, (4) **9**, 466. Prunier, *Compt. rend.*, 1873, **76**, 1410; *Chem. Soc. Abs.*, 1873, **26**, 1014; *Bull. soc. chim.*, 1873, (2) **20**, 72; *Ann. chim.*, 1879, (5) **17**, 17.

[205] *Ber.*, 1873, **6**, 70; *Bull. soc. chim.*, 1873, **19**, 145.

[206] *J.C.S.*, 1886, **49**, 74. *Cf.* Grimaux and Cloez, *Compt. rend.*, 1887, **104**, 118; *Chem. Soc. Abs.*, 1887, **52**, 352. Brochet, *Compt. rend.*, 1892, **114**, 601; *Chem. Soc. Abs.*, 1892, **62**, 797.

[207] Norton and Noyes, *Amer. Chem. J.*, 1886, **8**, 362.

[208] Noyes, *Jahresberichte*, 1888, 806.

[209] Norton and Andrews, *Amer. Chem. J.*, 1886, **8**, 4. von Stepsky, *Monatsh.*, 1902, **23**, 773; *Chem. Soc. Abs.*, 1903, **84** (1), 61.

[210] Ipatiev, *J. prakt. Chem.*, 1903, (2) **67**, 420; *Chem. Soc. Abs.*, 1903, **84** (1), 453.

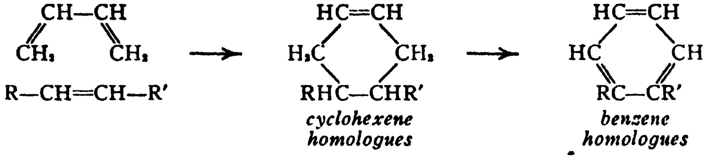
[211] Caventou, *Ann.*, 1863, **127**, 93. Thiele, *Ann.*, 1899, **308**, 333; *Chem. Soc. Abs.*, 1900, **78** (1), 2.

[212] Staudinger, Endle and Herold, *Ber.*, 1913, **46**, 2467.

[213] *J.A.C.S.*, 1922, **44**, 2036.

[214] *J.C.S.*, 1930, 1819.

thus pictured as depending upon a condensation of butadiene with olefins. Such condensations may be represented thus:



(R and R' may be either hydrogen or alkyl groups)

As previously mentioned, butadiene has been found among the products of the pyrolysis of numerous hydrocarbons including methane, ethane, propylene, cyclohexane, and many others. It is also present in Pintsch gas, Blau gas and oil gas and in ordinary high-temperature cracking gases.[215] Systematic experiments on the production of butadiene by the pyrolysis of ethylene at various temperatures were carried out by Zanetti, Suydam and Offner,[216] who found that, with a constant heating period of 0.8 minute, the percentage yield of butadiene increased from 0.08 at 600° C. to a maximum of 0.96 at 750° C. Beyond this latter temperature the yield rapidly declined. Frolich, Simard and White[217] have determined the proportions of butadiene formed in the pyrolysis of propane, butane, ethylene, propylene and cyclohexane at atmospheric pressure and at various temperatures in an apparatus consisting of a quartz tube about 38 cm. in length and 2.5 cm. diameter. On passing propane through this tube at the rate of 27 liters per hour a maximum yield of butadiene of 0.90 mole per cent (based on propane decomposed) occurred at 727° C. Butane, using the same gas rate, gave an optimum yield of 3.12 mole per cent at 727° C. Propylene (containing 86.8 per cent of nitrogen as a diluent and passed at a rate of 20 liters per hour) gave 3.31 mole per cent of butadiene at 728° C. A single experiment with cyclohexane (41.8 cc. per hour) at 654° C. gave a very high yield of 20.60 mole per cent, based on the cyclohexane decomposed. It is evident, therefore, that the cyclohexanes are suitable starting materials for the production of butadiene by pyrolysis.

OTHER METHODS FOR THE PRODUCTION OF DIOLEFINS BY PYROLYSIS

Most of the methods for making butadiene by pyrolysis are, just as in the case of isoprene, alike in their essentials. The thermal treatment is usually carried out at temperatures ranging from approximately 450° C. to 800° C., under atmospheric or reduced pressures, and, in some instances, in the presence of various contact materials.[218] The differences between the various processes appear to be chiefly in the raw materials. In addition to the various hydrocarbons, alcohols, fats, esters and other substances have yielded butadiene on heat treatment. Of the hydrocarbons, many petroleum fractions,[219] tetrahydrobenzene,[220] cyclohexane,[221] cyclopentane,[222] dipentene or its isomers and polymerized butadiene [223] have been proposed. Various alcohols suggested include 1,3-butanediol,[224] normal and secondary butanol,[225] fusel oil,[226] many glycols [227] and cyclohexanol.[228] Olefin oxides,[229] oleic acid, and its isomers, esters, particularly fats,[230] and acetals [231] have yielded butadiene. Other methods include the polymerization of ethylene in the presence of catalysts [232] and the incomplete combustion of certain organic materials.[233] Other methods for the production of diolefins are described in Chapter 27.

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[215] See, for example, Romoli-Venturi, *Annali Chim. Appl.*, 1930, **20**, 18; *Brit. Chem. Abs.* **B**, 1930, 357.

[216] *Loc. cit.*

[217] *Ind. Eng. Chem.*, 1930, **22**, 240.

[218] Ostromislensky (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1472; *J.S.C.I.*, 1916, **35**, 69; *Chem. Abs.*, 1916, **10**, 3178; *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1947; *Chem. Abs.*, 1916, **10**, 1340) has investigated a number of methods for obtaining butadiene, isoprene, piperylene and dimethylbutadiene.

[219] Farbenfabrik, vorm. F. Bayer and Co., French Patent 437,487, 1911; *Chem. Abs.*, 1912, **6**, 2548. German Patent 251,217, 1911; *Chem. Abs.*, 1913, **7**, 427. German Patent 283,162, 1913; *Chem. Abs.*, 1915, **9**, 2608. German Patent 262,884, 1912; *Chem. Abs.*, 1913, **7**, 3674. British Patent 251, 1912; *Chem. Abs.*, 1913, **7**, 2127. British Patent 4,076, 1913; *Chem. Abs.*, 1914, **8**, 2816. Addition 17,873, 1913, to French Patent 425,967; *Chem. Abs.*, 1915, **9**, 396.

Engler and Staudinger, *Ber.*, 1913, **46**, 2468. Also German Patent 265,172, 1912; *Chem. Abs.*, 1914, **8**, 586.

[220] Schmidt, U. S. Patent 1,070,294, Aug. 12, 1913; *Chem. Abs.*, 1913, **7**, 3424.

Considerable interest has been manifested in the production of diolefins by the pyrolysis of petroleum. Mersereau [234] obtained diolefins from petroleum hydrocarbons (particularly those boiling above 150° C. and containing 10 to 20 carbon atoms per molecule) by subjecting them to temperatures of 600° to 800° C. The products of pyrolysis are rapidly cooled to retard further reaction and to condense oil vapors, and the condensed hydrocarbons are mixed with fresh materials and returned to the cracking chamber. The gaseous products are reported to contain 8 to 9 per cent diolefins (principally butadiene), which are separated in one of several ways, e.g., by cooling and compression, by absorption in cooled low-cold-test gas oils, or by the action of various chemical reagents such as solutions of mercuric salts or liquid sulphur dioxide. The best method of recovering the diolefins Mersereau considered to be scrubbing the gas with wash oil at about —32° C. From the cold wash oil the diolefins are released by warming and liquefied by compression and cooling. The residual gas (containing 40 to 50 per cent olefins, 4 to 5 per cent of acetylenes, and a residue of saturated gases) may be subjected to further cracking.

Bysow [235] subjected the vapors of naphtha or other fractions or residues, preheated to 300° to 400° C., to pyrolysis under reduced pressure in a short reaction zone maintained at 750° to 1000° C. in the presence of iron, nickel or aluminum catalysts. The products are cooled rapidly. The pyrolysis may be carried out also in the presence of inert gases. The unsaturated hydrocarbons so obtained are capable of polymerization to rubber-like substances.

Natural or synthetic hydrocarbons, containing more than four carbon atoms per molecule, can be converted into olefins or diolefins having a smaller number of carbon atoms by bringing their vapors at temperatures of 600° C. or higher into contact with catalysts consisting of the difficultly reducible oxides of scandium, titanium, lanthanum, tungsten, molybdenum, thorium or uranium.[236] Alternatively, vaporized paraffins, olefins or alicyclic hydrocarbons may be passed at 640° to 720° C. over lustrous carbon deposited on difficultly reducible oxides such as magnesia, lime, baryta, quartz, or metals such as chromium.[237] Thus, cyclohexane at 650° C. gives 90 per cent unsaturated olefins, chiefly butadiene and ethylene, and American petroleum at 700° to 720° C. yields 80 per cent, of which one-fifth is butadiene.

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[221] Hofmann, Coutelle and Tank, U. S. Patent 1,050,077, Jan. 7, 1913; assigned to Farbenfabrik. vorm. F. Bayer and Co.; *Chem. Abs.*, 1913, 7, 906; Schmidt, Treppenhauer, Grosskinsky and Fischer, U. S. Patent 1,900,739, Mar. 7, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 2961.

[222] Farbenfabr. vorm. F. Bayer and Co., German Patents 248,738, 1911, and 262,553, 1912; *Chem. Abs.*, 1913, 7, 1426, 3425.

[223] Ostromislensky, British Patent 6,301, 1912; *Chem. Abs.*, 1913, 7, 3038. Also Farbenfabr. vorm. F. Bayer and Co., German Patent 282,817, 1912; *Chem. Abs.*, 1915, 9, 2608.

[224] Farbenfabr. vorm. F. Bayer and Co., British Patent 8,871, 1912; *Chem. Abs.*, 1913, 7, 3424. Hofmann, Delbrück, Köhler, and Meisenburg, U. S. Patent 1,179,408, April 18, 1916; *Chem. Abs.*, 1916, 10, 1717.

[225] Farbenfabr. vorm. F. Bayer and Co., German Patent 264,264, 1912; *Chem. Abs.*, 1914, 8, 267.

[226] Nauck, German Patent 264,902, 1912; *Chem. Abs.*, 1914, 8, 267.

[227] Kyriakides, *J.A.C.S.*, 1914, 36, 980. Kyriakides and Earle, U. S. Patents 1,033 327 and 1,033,328, July 23, 1912; *Chem. Abs.*, 1912, 6, 2696.

[228] Hofmann and Tank, U. S. Patent 1,010,405, Nov. 28, 1911; assigned to Farbenfabr. vorm. F. Bayer and Co.; *Chem. Abs.*, 1912, 6, 413. Farbenfabr. vorm. F. Bayer and Co., British Patent 27,555, 1910; *Chem. Abs.*, 1912, 6, 1499; German Patent 241,895, 1910; *Chem. Abs.*, 1912, 6, 2291.

[229] Matthews and Strange, British Patent 12,771, 1912; *Chem. Abs.*, 1913, 7, 3849.

[230] Gerlach and Koetschau, German Patent 267,079, 1912; *Chem. Abs.*, 1914, 8, 833.

[231] Ostromislensky and Kelbasinsky, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 123; *Chem. Abs.*, 1914, 8, 1965.

[232] Perkin and Matthews, British Patent 17,235, 1912; *Chem. Abs.*, 1914, 8, 433.

[233] Farbenfabr. vorm. F. Bayer and Co., German Patent 278,647, 1913; *Chem. Abs.*, 1915, 9, 1136.

[234] U. S. Patent 1,282,906, Oct. 29, 1918; assigned to Chemical Development Co.; *Chem. Abs.*, 1919, 13, 185.

[235] British Patent 297,231, 1927; *Brit. Chem. Abs.* B, 1928, 843.

In the pyrolytic decomposition of paraffins to butadiene using silica, silicates, noble metals or the catalysts mentioned above, improved yields are obtained when the starting materials are diluted with at least half their volume of steam.[238] The best apparatus is that made of or lined with metals which do not cause deposition of carbon: chromium, vanadium, manganese, or alloys such as highly alloyed steels containing considerable proportions of chromium, nickel, vanadium, manganese, cobalt, molybdenum, or tungsten.

Various other catalysts for the decomposition of acyclic or cyclic paraffins and higher olefins to yield butadiene and isoprene have also been considered.[239] The pyrolysis is usually carried out above 600° C. and the apparatus may be constructed of refractory metals or alloyed steels (such as those just mentioned above) or of Krupp V2A steel. Iron apparatus may be used if coated with chromium, copper, graphite, aluminum, or a noble metal. Thus, the decomposition of tetrahydrobenzene and of cyclohexane can be conducted in an apparatus of this type at 650° to 700° C. in a current of nitrogen and in contact with magnesia. The metal surfaces of the apparatus may be covered also with firmly adhering melts or sinters of inorganic compounds, such as silicates, phosphates, or borates with or without further additions of chromium, manganese, or copper. The object of these various materials is to suppress carbon formation as far as possible. One volume of steam to 2 volumes of hydrocarbon may be used. For example, a mixture of cyclohexane (2 vols.) and steam (1 vol.) is passed over granular lime at 680° C. to yield butadiene, propylene and other unsaturated hydrocarbons. A 65 per cent yield of butadiene is obtained, according to Schmidt, Grosskinsky and Niemann.[240]

The production of diolefins by heating acetylene and olefin hydrocarbons together in molecular proportions for an optimum period in the presence of catalysts, such as anhydrous alkali hydroxides, has been suggested.[241] If either the pressure, time of reaction, or the temperature be increased, then polymerization products of the diolefins may be obtained in a single stage. As an illustration, a mixture of acetylene and propylene in approximately molecular proportions is forced at 3 to 15 atmospheres pressure into a thick-walled spiral tube or autoclave heated to 350° to 450° C. The spiral is provided with a check valve at the inlet and an outlet valve which can be regulated to release the gases at any desired pressure. The escaping gases are cooled and the diolefins condense. Unchanged gas is recirculated through the apparatus. By using an indifferent gas as a diluent to increase the pressure to, say, 30 atmospheres, the yield of diolefin, in the present instance isoprene, is said to be increased to 85 per cent of the theoretical. When the operation is performed in an autoclave and the heating is continued for ten to fifteen hours at 55 to 65 atmospheres pressure the diolefin undergoes polymerization to rubber-like substances and intermediate products which may be of use in varnish and as turpentine substitutes.

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[236] I. G. Farbenindustrie A.-G., British Patent 297,398, 1927; *Chem. Abs.*, 1929, **23**, 2722.

[237] I. G. Farbenindustrie A.-G., British Patent 303,998, 1927; *Chem. Abs.*, 1929, **23**, 4483. *Cf.* Herrmann and Baum, Canadian Patent 279,622, 1928; *Chem. Abs.*, 1928, **22**, 2755.

[238] I. G. Farbenindustrie A.-G., British Patent 307,945, 1927; *Chem. Abs.*, 1930, **24**, 127.

[239] I. G. Farbenindustrie, A.-G., British Patents 317,359 and 317,303, 1928; *Chem. Abs.*, 1930. **24**, 2139.

[240] U. S. Patent 1,732,381, Oct. 22, 1929; *Chem. Abs.*, 1930, **24**, 127; German Patent 533,778, 1927; *Chem. Abs.*, 1932, **26**, 734. Both patents assigned to I. G. Farbenindustrie A.-G. See also French Patent 653,600, 1928; *Chem. Abs.*, 1929, **23**, 3715.

[241] H. Otto Traun's Forschungslaboratorium G.m.b.H., British Patent 156,116, 1922; *J.C.S.*, 1922, **122** (1), 515. See also I. G. Farbenindustrie A.-G., French Patent 666,611, 1929; *Chem. Abs.*, 1930. **24**, 1389.

The indirect preparation of isoprene from acetylene by a series of reactions involving the successive synthesis of acetaldehyde, aldol, 1,3-butylene glycol, methyl ethyl ketone, 2-methyl-3-keto-butanol, 2-methyl-1,3-butylene glycol, and finally isoprene has also been described.[242] Dubosc [243] outlined a similar procedure for making butadiene, and subsequently synthetic rubber from it. The steps include the formation of acetylene (from calcium carbide), acetaldehyde, aldol, butylene glycol, and lastly butadiene.

The thermal decomposition or dehydration of the lower aliphatic alcohols to yield diolefins has been known for many years. Lebedev [244] proposed the dehydration of methyl, ethyl or propyl alcohol at 400° C. in the presence of such catalysts as alumina or zinc oxide. The products may be passed into bromine and the tetrabromide thus formed may be separated by fractional distillation and converted into butadiene by reduction The use of 1,3-butylene glycol for the preparation of butadiene has also been suggested.[245] Its dehydration is carried out by conducting the vapors of the glycol together with water vapor over heated catalysts (acid bismuth orthophosphate, neutral pyro- or orthophosphates of magnesium or the alkaline earth metals, a mixture of calcium and ammonium phosphates, or primary sodium phosphate and either graphite or phosphoric acid). By dehydration, ethylene can be obtained from ethyl alcohol, cyclohexene from cyclohexanol, and isoprene from 2-methyl-1,3-butylene glycol. Unsaturated alcohols have also been used.[246]

That lower molecular weight olefins can be condensed to those of higher molecular weight has long been known.[247] Häuber,[248] for example, suggested heating the lower olefins to 250° C. in the presence of silicon to effect the formation of higher olefins. Feiler [249] subjected the lower olefins to high-temperature electrical discharges in a closed cycle with continual removal of the products (olefins and diolefins) by cooling. Butadiene has been formed by passing a mixture of 1- and 2-butenes (obtained by the dehydration of butyl alcohol vapor at 320° C. over bauxite) diluted with nitrogen through a tube packed with calcium oxide and heated to 700° C.[249a]

It is interesting to note that butadiene may also be obtained by the partial hydrogenation of diacetylene in the presence of catalysts,[250] and by the reduction of diacetylene with chromous chloride solution.[251]

SEPARATION OF THE DIOLEFINS

For the separation of diolefins (particularly those of low molecular weight) from mixtures, use is generally made of certain materials exerting a preferential solvent action on these hydrocarbons. Sulphur dioxide is especially appropriate for this purpose, but the effect is probably not purely solvent action since compound formation undoubtedly occurs. For instance, Matthews and Elder[252] formed addition products of various olefins with sulphur dioxide and Staudinger[253] obtained monomeric solid reaction products by treating butadiene hydrocarbons with liquid sulphur dioxide at room temperature in the presence of 1 per cent hydroquinone as a stabilizing agent. A method for the separation of diolefins from hydrocarbon mixtures by the action of sulphur dioxide at 100° C. has been described by Perkins.[254] The process may be carried on continuously by constantly removing a portion of the reaction mixture and the diolefin-sulphur dioxide addition products are separated by distillation. The product obtained from 1,3-butadiene and sulphur dioxide is a crystalline solid (m.p., 65° C.) which is decomposed into its components by heating at temperatures exceeding 120° C. According to Plauson[255] acetone saturated with sulphur dioxide is an excellent reagent for diolefins and forms insoluble addition compounds. The latter can be filtered off as precipitates from which the diolefins may be regenerated by heating. The reactions of diolefins with sulphur dioxide and other reagents are discussed more fully in Chapter 27.

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[242] I. G. Farbenindustrie A.-G., British Patent 320,362, 1928; *Chem. Abs.*, 1930, 24, 2640.

[243] *Bull. soc. ind. Rouen,* 1926, 54, 223; *Chem. Abs.*, 1927, 21, 673.

[244] British Patent 331,482, 1929; *Chem. Abs.*, 1931, 25, 115. *Cf.* I. G. Farbenindustrie A.-G., German Patent 544,290, 1927; *Chem. Abs.*, 1932, 26, 2471.

[245] I. G. Farbenindustrie A.-G., British Patent 317,500, 1928; *Chem. Abs.*, 1930, 24, 2139.

[246] I. G. Farbenindustrie A.-G., British Patent 345,270, 1928; *Chem. Abs.*, 1932, 26, 157.

[247] Perkin and Matthews, British Patent, 17,235, 1912; *Chem. Abs.*, 1914, 8, 433.

[248] German Patent 543,110, 1929; assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1932, 26, 2466.

[249] U. S. Patent 1,799,787, April 7, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 25, 3012.

[249a] I. G. Farbenindustrie A.-G., German Patent 544,290, 1929; *Chem. Abs.*, 1932, 26, 2471.

[250] Bolton and Downing, U. S. Patent 1,777,600. Oct. 7, 1930; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1930, 24, 5770.

[251] Baumann and Tanneberger. German Patent 540,003, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 1625.

The use of various organic liquids as solvents for the separation of diolefins by selective solution from gaseous or liquid mixtures containing monolefins or saturated hydrocarbons has been described.[256] The liquids suggested are glycol chlorohydrin, glycol mono- and di-acetates, glycol mono-methyl ether, glycerol di- and tri-acetates, lactic acid nitrile, diethyl tartrate, furfural and aromatic bases.

Certain metallic salts in aqueous solution or suspension, as is well known, possess an affinity for diolefins as well as for monolefins. The use of cuprous and silver salts (e.g., cuprous chloride and silver nitrate) for the separation of diolefins, particularly butadiene, in gaseous mixtures has been recommended by Feiler.[257] Under certain conditions the double compound of the diolefin with the metallic salt precipitates, and from this the diolefin may be liberated by warming.

Carbon monoxide and diolefins can be removed from gaseous mixtures by absorption in a solution of cuprous chloride.[258] Hydroxylamine hydrochloride, hydroquinone, sulphites or stannous chloride may be added to such solutions to prevent oxidation of the cuprous to cupric salts. Alkali, alkaline earth or magnesium salts dissolved in water or alcohol may be used as neutral solvents. The formation of a precipitate is obviated in such solutions and the absorbed carbon monoxide and diolefins may be recovered by warming the liquid to 40° to 80° C., under reduced pressure, if necessary.

For the separation of butadiene hydrocarbons from isobutylene and similar olefins containing a tertiary carbon atom, advantage may be taken of the relatively higher rate of absorption of the latter in sulphuric acid of the proper concentration,[259] 60 to 70 per cent being recommended.[260]

[252] British Patent 11,635, 1914; *Chem. Abs.*, 1915, **9**, 2971.

[253] British Patent 361,341, 1930; *Brit. Chem. Abs.* **B**, 1932, 301.

[254] Canadian Patent 329,043, 1933; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 1358.

[255] U. S. Patent 1,436,289, Nov. 21, 1922; *Chem. Abs.*, 1923, **17**, 627. H. O. Traun's Forschungslaboratorium G.m.b.H., British Patent 156,123, 1920; *J.S.C.I.*, 1922, **41**, 403A.

[256] I. G. Farbenindustrie A.-G., British Patent 319,025, 1928; *Chem. Abs.*, 1930, **24**, 2468. Schmidt and Grosskinsky, U. S. Patent 1,882,978, Oct. 18, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 737. U. S. Patent 1,919,752, July 25, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4813.

[257] U. S. Patent 1,795,549, March 10. 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 2435. British Patent 303,323, 1928; *Brit. Chem. Abs.* **B**, 1929, 199.

[258] Bataafsche Petroleum Maatschappij, British Patent 359,234, 1929; *Chem. Abs.*, 1932, **26**, 4894. French Patent 705,214, 1930; *Chem. Abs.*, 1931, **25**, 5223.

[259] I. G. Farbenindustrie A.-G., French Patent 703,743, 1930; *Chem. Abs.*, 1931, **25**, 4555.

[260] Bataafsche Petroleum Maatschappij, French Patent 737,743, 1932; *Chem. Abs.*, 1933, **27**, 1638. The absorption of olefins in sulphuric acid is discussed in greater detail in Chapters 12, 14, 16, and 49.

Chapter 5

Production of Aromatic Hydrocarbons by Pyrolysis of Petroleum Hydrocarbons

It has long been known that aromatic hydrocarbons may be produced in quantity by subjecting other hydrocarbons to pyrolysis at fairly high temperatures. As early as 1860 the presence of aromatic hydrocarbons was demonstrated in the tar obtained as a by-product in the manufacture of oil gas by high-temperature pyrolysis of mineral oils. The aromatic hydrocarbons in coal tar, made by the high-temperature carbonization of bituminous coal, have formed the raw materials for the manufacture of a wide variety of synthetic organic substances.

The World War created a great demand for toluene for the manufacture of the explosive, trinitrotoluene (TNT), and attempts were made to augment the supply derived from coal tar by cracking petroleum hydrocarbons at high temperatures. Toward the end of the war aromatic hydrocarbons were being produced from petroleum by cracking and several processes were in operation. As has been mentioned in Chapter 1, efforts were made at the same time to obtain toluene directly from highly aromatic crude petroleums, particularly those from Borneo. Very few, if any, crude oils, however, contain sufficient toluene initially to insure the success of this operation.

After the World War, interest in the synthesis of aromatic hydrocarbons from petroleum waned considerably, but during the last few years of the decade 1920-1930 a renewal of interest in this problem was manifest. This is particularly true of processes which utilize as raw material the abundant supplies of dry natural gas, otherwise largely wasted or inefficiently used. Two circumstances have combined to focus the attention of the petroleum industry on the production of aromatic hydrocarbons from gaseous aliphatic hydrocarbons, especially from methane and its immediate homologues. One is the increasing demand for the rigorous conservation of natural gas resources. The other is the possibility of obtaining aromatic hydrocarbons (which are excellent anti-knock materials) from natural gas for blending with gasolines to increase their anti-detonating qualities. The latter particularly has aroused wide interest. In those countries dependent upon others for supplies of liquid fuels, research on the conversion of methane and other gaseous hydrocarbons present in coal gas and coke-oven gas into liquid hydrocarbons (benzene and toluene) is being vigorously pursued. This is notably true of Great Britain and Germany.

PRODUCTION OF AROMATIC HYDROCARBONS FROM PETROLEUM

The effect of temperature on the pyrolysis of petroleum distillates varies somewhat with the nature and the composition of the raw material, but in general, it can be said: (1) temperatures from 500° to about 600° C. yield principally mixtures of olefin and paraffin hydrocarbons; (2) at about 650° C. and above, diolefins are formed; and (3) at 700° C. and slightly above, aromatic hydrocarbons are produced in quantity. At higher temperatures much hydrogen, methane, carbon and highly condensed aromatic hydrocarbons are obtained.

According to Rittmann,[1] the highest yield of aromatic hydrocarbons from pyrolysis of petroleum distillates occurs in the region of 650° to 700° C. These optimum temperatures, however, are dependent to some extent upon the nature of the oil, the pressure, the size and shape of the reaction space, and the rate of oil feed (i.e., the duration of the reaction).

In the pyrolysis of most petroleum distillates (with the possible exception of those containing large proportions of cyclohexane derivatives) the production of aromatic hydrocarbons is not the primary reaction. It is now well established that the formation of olefins and diolefins precedes that of aromatics and there is much evidence to show that the diolefins of the butadiene type are the immediate precursors of aromatic hydrocarbons. It was formerly believed that acetylene was the intermediate in the formation of aromatics during cracking. Although this may be true in the re-composition of certain gaseous hydrocarbons requiring temperatures of 800° C. and over, it is doubtful whether perceptible quantities of acetylene could be formed at temperatures at which the formation of aromatic hydrocarbons is already rapid. The fact that only negligible proportions of acetylene have been noted during the pyrolysis of hydrocarbons at 700° C. and below is, of course, not conclusive evidence against the acetylene theory of aromatic formation, since acetylene might be assumed to polymerize immediately to yield aromatics. Nevertheless, thermodynamic calculations lead to the conclusion that acetylene cannot be produced in any amount at temperatures below 800° C.

According to Smolenski, Turowicz and Dobrowolski,[2] the pyrolysis of crude Baku petroleum to yield appreciable quantities of aromatic hydrocarbons requires temperatures of 680° to 720° C. Among the products obtained at these temperatures the following hydrocarbons were identified: benzene, toluene, xylenes, naphthalene and anthracene. Above 800° C. degradation to carbon, hydrogen and methane was found to be increasingly predominant.

The thermal decomposition of petroleum distillates into aromatic hydrocarbons occurs at temperatures considerably exceeding those required for ordinary cracking operations for the production of gasoline, and consequently there is always a simultaneous formation of much permanent gas and carbonaceous material. Moreover, the separation of the aromatic hydrocarbons from the products of the pyrolysis of petroleum distillates is rendered difficult by the simultaneous occurrence of olefins and diolefins having boiling points approximating those of the aromatics. As a consequence, much sulphuric acid is required to refine the crude benzene. Too high temperatures and too heavy raw materials give poor yields of benzene, and particularly of toluene and xylene. The cracking temperature, therefore, should not exceed 700° C. Even at this temperature olefins and diolefins are important constituents of the reaction products. The yields of aromatics are variously stated by different observers. Rittman gave the yields from his process as 6 to 8 per cent each of benzene and toluene, and 4 to 6 per cent of xylene.

It is questionable whether specific catalysts are of any real value in the pyrolytic formation of aromatics. At first thought it might appear that dehydrogenating catalysts would be useful in this connection, but it should be noted that aromatics are usually formed as the result of a complex series of reactions in which dehydrogenation, polymerization and ring closure (cyclicization) may be specifically distinguished. Of course, it is known that cyclohexane derivatives can be dehydrogenated to benzene derivatives in the presence of certain catalysts, particularly nickel and palladium black. However, at the comparatively high temperatures necessary to convert aliphatic hydrocarbons to aromatics such catalysts as nickel tend to increase the yield of carbon, hydrogen and methane. Thus, Ostromislensky and Burshanadse[3] showed that crude Russian petroleum, when passed over reduced nickel at 600° to 700° C., completely disintegrated to hydrogen, methane and a carbonaceous residue. Similarly, Zanetti[4] reported that the presence of nickel did not favor the formation of aromatic hydrocarbons during the pyrolysis of propane-butane mixtures. Davidson[5] found that iron, nickel and cobalt are negative catalysts for the formation of aromatics by the pyrolysis of ethane-propane mixtures and that they accelerate the reactions producing carbon and hydrogen. On the other hand, Ostromislensky and Burshanadse[6] observed that the conversion of naphtha into aromatic hydrocarbons at 700° C. is improved by the presence of a spiral of iron gauze, a yield of 10.9 per cent of benzene having been obtained as against 7.5 per cent of benzene under the same conditions without the iron. Uhde[7] suggested heating petroleum or other hydrocarbons under pressure in intimate mixture with finely divided metals to produce liquid hydrocarbons. Iron with water may be used, the iron being regenerated by the hydrogen produced.

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[1] *Ind. Eng. Chem.*, 1915, 7, 945, 1019; *Met. Chem. Eng.*, 1916, 14, 15.

[2] *Przemysl Chem.*, 1921, 5, 201, 237; *Chem. Zentr.*, 1922, 2, 899; *J.S.C.I.*, 1922, 41, 402A.

By distilling Zistersdorf petroleum to 300° C. in the presence of 0.5 per cent of active carbon, the fraction boiling to 200° C. increased in quantity from 1.4 to 8.1 per cent and the fraction boiling to 300° C., from 11.4 per cent to 45 per cent.[7a] No further increase was obtained by redistilling this product in the presence of active carbon with or without the addition of silicon dioxide gel.

The effect of cracking a spray oil at various temperatures and at constant rates of flow was investigated by Groll.[7b] The oil consisted of 94 per cent volatile matter and boiled between 277° and 365° C. On cracking at 600° C., the product was a complex mixture of all types of hydrocarbons. From the indications, aromatic compounds are not formed at this temperature. The substances from the distillate boiling between 65° and 70° C. were hexylenes.

At 650° C. indications of aromatics first appeared. Benzene, toluene and xylene were obtained in about equal quantities, but mixed with a large amount of aliphatic hydrocarbons. The presence of hexylenes was still noticeable. At 700° C. the yield of aromatics became more predominant, with the yield of benzene exceeding that of toluene, and a smaller amount of xylene. The total yield of liquid and solid products approaches its minimum at this temperature and the residue of the tar after distillation of the gasoline consists mainly of aromatic polycyclic hydrocarbons. Many of these have aliphatic side-chains.

From 725° to 825° C. the yields are fairly constant. The only changes brought about by further increase of temperature are the gradual disappearance of aliphatic hydrocarbons and the splitting of side-chains from the alkylated aromatics.

Varying the rate of flow of oil likewise varies the composition of the product. It was found that an increase at high temperature will favor products which correspond to those formed at a lower temperature with a smaller rate of flow.

The aromatic hydrocarbons produced in these pyrolytic processes, although resulting from a series of reactions, are themselves only intermediate products in a further sequence of changes. Given a sufficiently long heating period the aromatics initially formed will be converted into other substances and finally into hydrogen, methane and coke. The attainment of this ultimate condition is reached more rapidly in the presence of such catalysts as nickel. However, when a number of reactions can occur simultaneously it is possible by a proper choice of contact materials to catalyze one at the expense of the others, and in most of these hydrocarbon reactions in which the desired product is an intermediate in a whole sequence of changes, the time factor is always of importance.

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[3] *J. Russ. Phys.-Chem. Soc.*, 1910, **42**, 195; *Chem. Zentr.*, 1910, **1**, 1711.
[4] *Ind. Eng. Chem.*, 1916, **8**, 674.
[5] *Ind. Eng. Chem.*, 1918, **10**, 901.
[6] *J. Russ. Phys.-Chem. Soc.*, 1910, **42**, 195; *Chem. Zentr.*, 1910, **1**, 1711.
[7] French Patent 680,605, 1929; *Chem. Abs.*, 1930, **24**, 3897.
[7a] Diesenhammer, *Petroleum Z.*, 1933, **29** (17), 3.
[7b] *Ind. Eng. Chem.*, 1933, **25**, 784.

Differences in the nature of the oil subjected to pyrolysis appear to exert only a small influence on the yield of aromatic hydrocarbons, although those oils containing cyclic hydrocarbons (particularly cyclohexane derivatives) are probably somewhat more amenable to conversion. For this reason petroleum distillates containing appreciable quantities of cyclic hydrocarbons were utilized as raw materials in some of the processes for making toluene.

Weiderpass[8] has studied the conversion of Esthonian shale oil distillates into aromatic hydrocarbons by vapor-phase cracking in a tinned iron tube at 750° C. The light fraction (boiling up to 170° C.) of the products was equivalent to about 30.2 per cent of the original shale oil, or about 39.1 per cent of the products, and consisted mainly of aromatic hydrocarbons. At the same time a large proportion of permanent gas, having a calorific value of 1200 B.t.u. per cubic foot, was obtained.

The cracking of Emba crude oil in the presence of aluminum chloride was studied by Zelinskii and Mikhlin.[8a] The oil was first dehydrated by heating to 110° C. and then cracked at atmospheric pressure in the presence of 10 per cent of aluminum chloride. The yields were 48 per cent of gasoline boiling between 50° and 200° C., 15 per cent of a fraction boiling between 200° and 300° C., and 18 per cent boiling above 300° C. The gasoline fraction (50°-200° C.) contained 11 per cent of aromatic compounds. It was treated with fuming sulphuric acid to remove aromatic compounds and then subjected to catalytic dehydrogenation. The resultant material contained 8.5 per cent of aromatic compounds formed as a result of the dehydrogenation of the hydroaromatic compounds present.

Interest was aroused near the close of the World War when several processes were put into operation in the United States and elsewhere for the production of toluene and other aromatics by the pyrolysis of petroleum fractions.

In the Hall process[9] the oil under treatment is passed through a continuous coil of about 600 feet of tubing of 1 inch internal diameter at temperatures and pressures which vary according to the desired products. The oil is vaporized and the vapors attain a speed of about 5000-6000 linear feet per minute in passing through the end of the coil where the temperature is greatest. At the exit the vapors are suddenly expanded into a tube of much greater diameter and the pressure drops to atmospheric. At this point the major portion of the pyrolysis reactions occur, accompanied by some carbon deposition. The vapors next pass into a series of dephlegmators where separation into various fractions is accomplished.

When working for motor fuel a temperature of 550° to 600° C. is maintained at the exit ends of the tubes. On the other hand when operating for aromatics (for the production of which the plant can be readily adapted), the temperatures and pressures employed are necessarily higher (about 750° C. and 105 to 110 pounds per square inch, respectively). A good yield of gas of high calorific value is simultaneously produced. The Hall process is said to give a readily refined fuel containing as high as 18.5 per cent of benzene, 17.5 per cent of toluene, and about 6.0 per cent of xylenes.

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[8] *Sitzber. Naturforsch. Ges. Univ. Tartu*, 1927, 34, 143.

[8a] *J. Applied Chem. (U.S.S.R.)*, 1933, 6, 16; *Chem. Abs.*, 1933, **27**, 5176.

[9] U. S. Patents 1,105,772, Aug. 4, 1914; 1,175,909 and 1,175,910, Mar. 4, 1916; 1,194,289, Aug. 8, 1916; 1,239,099 and 1,239,100, Sept. 4, 1917; 1,242.795 and 1,242,796, Oct. 9, 1917; 1,247,671, Nov. 27, 1917; 1,261,930, Apr. 9, 1918; 1,285,136, Nov. 19, 1918. *J. Inst. Pet. Tech.*, 1915, 1, 147.

The Rittman process[10] was based on investigations carried out by the United States Bureau of Mines[11] and is adapted to the manufacture of gasoline or of benzene and toluene from petroleum. As finally adopted for commercial purposes the benzene-toluene plant consisted of six furnaces each heated by gas-burners and containing 2 rows of 5 vertical reaction tubes (11½ feet long and 8 inches in diameter). Each tube was fitted with a separate oil supply and condenser. Carbon was removed by a special wiping-chain attached spirally to a rotating rod passing up through the center of each tube. For the production of aromatic hydrocarbons the temperature was about 700° C., the pressure about 150 lbs. per sq. in. and the oil was fed to each tube at the rate of 15 gallons per hour. The reactions were found to be practically independent of the nature of the oil cracked, although solvent naphthas and light oil distillates from coal tar gave the best results. The large amount of high calorific value gas produced was sufficient for the fuel requirements of the plant. The following yields from petroleum have been reported: benzene 6 to 8 per cent, toluene 6 to 8 per cent, xylenes 4 to 6 per cent, gasoline 6 to 8 per cent, creosote oil and pitch (including higher aromatic hydrocarbons) 23 to 30 per cent, carbon 3 to 5 per cent, and permanent gas 45 to 60 per cent of the original oil.

According to Lomax, Dunstan and Thole[12] the benzene-toluene fraction produced by the Rittman process contains considerable proportions of non-benzenoid hydrocarbons, unattacked by sulphuric acid, so that the preparation of TNT from the toluene fraction of the cracked product requires special methods. On the other hand, products obtained by the Hall process contain only relatively small proportions of non-aromatic hydrocarbons which are unattacked by concentrated sulphuric acid so that the direct nitration of the toluene fraction was not difficult.

Another process for making aromatic hydrocarbons from petroleum was that of the General Petroleum Corporation, by which a yield of about 6 per cent of toluene was obtained from a petroleum distillate, high in cyclic hydrocarbons, by thermal treatment under pressure. As far as is known, however, no complete account of this process has been given, but it was probably a modification of the vapor phase process developed by Washburn[13] and later acquired by the above company.[14]

PRODUCTION OF AROMATIC FROM SATURATED HYDROCARBONS

Aromatic hydrocarbons can be produced in quantity by the pyrolysis of a large variety of gaseous hydrocarbons at temperatures of 700° C. and over. It has long been known that ethylene and acetylene could be made to yield aromatic hydrocarbons by such treatment but investigations of the conversion of paraffin hydrocarbon gases, especially methane, an abundance of which occurs in natural gas, were not undertaken until much later. The possibility of converting the gaseous paraffins of natural gas into liquid aromatic hydrocarbons is of importance in connection with the conservation and more efficient utilization of that abundant material. In countries where natural gas does not occur to any extent the gaseous hydrocarbons of coal gas and coke-oven gas might be utilized for conversion into benzene and other aromatic hydrocarbons by pyrolytic processes. The aromatic liquids so produced are valuable, on account of their comparatively high antiknock values, for blending with straight-run gasolines. In the following discussion this utilization of the gaseous paraffins will be considered in some detail.

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[10] British Patents 9,162 and 9,163, 1915; *Chem. Abs.*, 1916, 10, 3156; *cf.* British Patent 13,100, 1915; *Chem. Abs.*, 1917, 11, 538.

[11] Rittman, Dutton and Dean, *U. S. Bur. Mines Bulletin* 114, 1916; *Chem. Abs.*, 1916, 10, 1425; Rittman, *Ind. Eng. Chem.*, 1915, 7, 945; *ibid.*, 1915, 7, 1014.

[12] *J. Inst. Pet. Tech.*, 1916-17, 3, 70.

[13] U. S. Patent 1,138,266, May 4, 1915.

[14] See Leslie, "Motor Fuels," Chemical Catalog Co., Inc., New York, 1923, 346.

AROMATIC HYDROCARBONS FROM METHANE

The conversion of methane into aromatic liquids and gaseous hydrocarbons was effected by Fischer,[15] who worked on the assumption that by shortening the heating period and controlling the rate of cooling, methane would not be decomposed into its elements but would yield labile residues, such as $\cdot CH_3$ $:CH_2$, and $:CH$, which would polymerize to higher hydrocarbons. When methane of varying degrees of purity was passed at high gas speeds through porcelain or quartz tubes heated to 1000° to 1200° C., he obtained considerable yields of higher hydrocarbons, chiefly aromatic. The duration of heating was of great importance. When a heating period of 60 seconds was employed complete decomposition to hydrogen and carbon occurred, and he preferred a period of about ⅓ of a second. The light oil from methane contained benzene, toluene, xylenes and naphthalene, together with unsaturated hydrocarbons. The tar was a dark brown fluid containing naphthalene and higher aromatic hydrocarbons and, in addition, more or less free carbon. Silicic acid, tungsten and molybdenum did not catalyze decomposition to carbon and hydrogen but iron and graphite did.

Later, Fischer and Pichler[16] found that maximum yields of benzene were obtained at a temperature of 1300° C. with a time of contact of 0.016 second, or by conducting methane through a series of tubes maintained at 1200° C. and removing the liquid materials after each heating. Above 1400° C. acetylene was the main product.

Similar results were obtained by Stanley and Nash[17] by passing pure methane at high gas rates through silica tubes heated at 1000° to 1200° C. The solid and liquid products were not examined in great detail but the gaseous products were subjected to a special investigation by low-temperature condensation methods. The best yield of higher hydrocarbons was obtained with a temperature of 1150° C. and a heating period of about 0.6 second. Under these conditions the yield of light oil and tar totaled 11.0 per cent, calculated on the methane used, and acetylene and ethylene in the reaction gas corresponded to 8.8 per cent of the methane. The yield of light oil was 4.8 per cent or 9.2 gallon per 1,000 cubic feet of methane. The use of comparatively long heating periods tended to cause methane to decompose almost exclusively into its elements, this tendency being greatly increased by the use of catalytically active materials such as iron and nickel.

The pyrolysis of methane at temperatures up to 1050° C. in tubular reaction chambers of quartz, porcelain, copper and iron was examined by Wheeler and

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[15] *Brennstoff-Chem.*, 1928, 9, 309.

[16] *Brennstoff-Chem.*, 1932, 13, 381. See also Fischer and Hintermaier, *Ges. Abhandl. Kenntnis Kohle*, 1930, 9, 678.

[17] *J.S.C.I.*, 1929, 48, 1T.

Wood.[18] A horizontal tube of quartz at 1050° C. gave the best yields of crude oil under these conditions and the yield of benzene was about 0.2 gallon per 1000 cubic feet of methane. Quartz and copper surfaces were found not to catalyze decomposition into carbon and hydrogen, but when an iron tube was used the methane was decomposed entirely into its elements. Dilution of the methane with nitrogen had little effect on the yield of aromatic hydrocarbons but, contrary to the experience of Fischer, dilution with hydrogen decreased the yield considerably. The gaseous products of the reaction were brominated and ethylene dibromide and butadiene tetrabromide were isolated.

The results obtained by Chamberlin and Bloom[19] on the pyrolysis of natural gas are somewhat at variance with those of preceding investigators. These differences can be accounted for by the fact that Chamberlin and Bloom employed natural gases containing appreciable proportions of ethane (3.4 to 23.3 per cent). The gas was thermally treated in tubes of silica, steel, copper, iron, nickel, monel metal and clay at temperatures as high as 900° C. Aromatic hydrocarbons (principally benzene, naphthalene and anthracene), acetylene, ethylene and other olefins, were all produced at temperatures below 900° C. The yield of benzene from natural gas amounted to 27 liters per 1000 cubic feet of gas. Fused silica, clay, copper and monel metal did not catalyze the formation of carbon and hydrogen to any extent, but iron and nickel readily decomposed methane into its elements. The observation was made that while certain forms of carbon catalyzed the decomposition of methane into its elements, the carbon made from natural gas at temperatures of 450° C., or higher, selectively converts gaseous paraffins into aromatic hydrocarbons. This activity is easily destroyed by partial oxidation or by the formation of carbon-metal compounds or graphitic carbon. In agreement with the results of Wheeler and others with pure methane, Chamberlin and Bloom found that the presence of hydrogen reduces the yield of oily products and when the concentration of hydrogen is 50 to 60 per cent of the gas treated the oil yield becomes negligible.

Vysoky[20] reported that benzene is produced during the pyrolytic decomposition of methane at 800° to 850° C., and that benzene formation is not greatly affected by the partial oxidation of methane in the presence or absence of copper catalysts.

DeRudder and Biedermann[21] studied the dissociation of methane at high temperatures and reduced pressures. This investigation, though not specifically directed toward the formation of aromatic hydrocarbons, throws much light on the mechanism of decomposition. Below 1000° C., the thermal decomposition of methane yielded only minute quantities of ethylene and no acetylene. The maximum quantity of ethylene (4 per cent of the methane) was produced at 1200° C. and 100 mm. pressure, and 2.5 per cent of acetylene was simultaneously formed. At 1300° C. and 100 mm. pressure, at 1400° C. and 50 mm., and at 1500° C. and 50 mm., no ethylene was obtained but the yields of acetylene were 6.6 per cent, 10.5 per cent and 14.5 per cent, respectively. The increased formation of acetylene with rising temperature was thus clearly demonstrated. The observation was made that nickel tubes gave products similar to those secured with tubes of quartz or Marquardt porcelain. Hydrogen chloride exerted no catalytic influence.

Padovani and Magaldi[22] found that dilution of methane with hydrogen increased the yield of unsaturated hydrocarbons during high-temperature pyrolysis.

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[18] *Fuel,* 1928, 7, 535.
[19] *Ind. Eng. Chem.,* 1929, 21, 945.
[20] *Paliva a Top.,* 1929, 11, 53; *Brit. Chem. Abs.* A, 1930, 735.
[21] *Compt. rend.,* 1930, 190, 1194; *Bull. soc. chim.,* 1930, (4) 47, 704.
[22] *Atti III cong. naz. chim. pura applicata,* 1930, 730; *Chem. Abs.,* 1931, 25, 3309.

This effect was reversed at high rates of flow of the gases, an observation which would appear to reconcile the difference between Fischer's conclusions and those of Wheeler and Wood.

Waterman and his co-workers [22a] studied the thermal decomposition of paraffin wax in the presence and in the absence of hydrogen at high pressures. It was concluded that the presence of hydrogen inhibits the formation of ring compounds, only one-seventh the quantity being formed as is formed in the absence of hydrogen.

Further experiments of Wheeler and Wood [23] were directed toward the elucidation of the mechanism of the formation of higher hydrocarbons from methane. In silica tubes at 1050° C., with heating periods of the order of 0.3 second, 84 per cent of the methane consumed was converted into higher hydrocarbons. Increasing the heating period resulted in decomposing more methane into carbon and hydrogen. The use of an iron tube led to the complete decomposition of methane into its elements (the carbon formed being of a bulky gritty nature) even at comparatively low temperatures. No difference could be detected in the formation of liquid hydrocarbons from methane in chrome-iron and in silica tubes. The carbon deposited on the silica or chrome-iron tubes was lustrous and foil-like, and its accumulation did not influence the course of the reaction. Wheeler and Wood observed that a large increase in the area of silica exposed per unit volume of gas had no appreciable effect on the rate or extent of ultimate decomposition. These investigators believed that the important reactions are homogeneous and take place throughout the volume of the gas as soon as the surface reaction has been inhibited by the formation of a protective layer of adsorbed hydrogen. This hydrogen layer is apparently not formed on iron and the surface reaction (formation of carbon and hydrogen) predominates. Static experiments in a silica bulb showed that rapid initial decomposition is chiefly a surface effect which is accelerated by packing the bulb with silica and does not proceed to a true equilibrium because of a protective hydrogen layer. On the other hand, Padovani [24] considered that increasing the heating surface is of much more importance than catalytic action. He was able to prepare high grade lampblacks (together with liquid aromatic hydrocarbons) in yields of 50 per cent or more by the pyrolysis of natural gas (98 per cent methane) or coke-oven gas (about 29 per cent methane and 58 per cent hydrogen) at temperatures of 1000° to 1300° C. Pyrolysis was effected without the aid of pressure or of catalysts.

A preliminary report on the production of liquid hydrocarbons by the pyrolysis of methane in a sillimanite reaction tube at high temperatures was presented by Smith, Grandone and Rall.[25] The following hydrocarbons were identified among the products of pyrolysis: ethylene, acetylene, benzene, naphthalene, anthracene and pyrene. Unsaturated liquids boiling above and below benzene, as well as liquids and solids of very high boiling points were also formed. While the addition of hydrogen diminished the total yield of higher hydrocarbons, the percentages of ethylene and of acetylene in the gaseous products were increased by diluting the methane with either hydrogen or nitrogen. As might be expected, the presence of ethane in the initial gas increased the yield of liquid products. The highest yields from 1000 cubic feet of methane were: about 0.3 gallon of benzene or light oil; 2.5 pounds of liquid tar containing 35 per cent of naphthalene and anthracene, together with a large amount of higher hydrocarbons; and 1200 cubic feet of gas consisting of 710 cubic feet of methane, 440 cubic feet of hydrogen, and 25 cubic feet each of ethylene and acetylene.

[22a] Waterman, Tulleners and Dooren, *Proc. Acad. Sci. Amsterdam*, 1932, **35**, 1063; *Chem. Abs.*, 1933, **27**, 655; Waterman, te Nuyl and Perquin, *J. Inst. Pet. Tech.*, 1929, **15**, 369; *Chem. Abs.*, 1929, **23**, 4812; Waterman, deKok and Tulleners, *J. Inst. Pet. Tech.*, 1932, **18**, 1007.

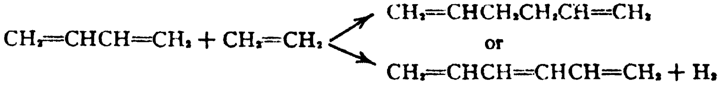
[23] *Fuel*, 1930, **9**, 567; *Brit. Chem. Abs.* **B**, 1931, 193. *Cf.* Holliday and Exell, *J.C.S.*, 1929, 1066.

[24] *Proc. 3rd Intern. Conf. Bituminous Coal*, 1932, **1**, 910; *Chem. Abs.*, 1932, **26**, 4935.

[25] *U. S. Bur. Mines, Rep. Investigations* 3143, 1931.

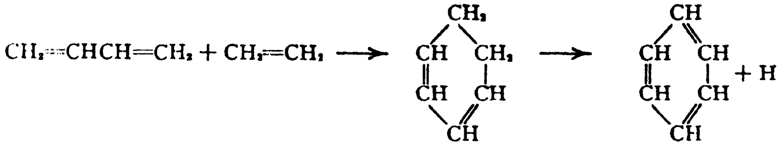
When the above results of the pyrolysis of methane are compared with corresponding ones obtained from its homologues, it is evident that methane requires much higher temperatures and produces much lower yields of liquid hydrocarbons. For these reasons, and in spite of the abundance of methane present in natural gas, it is doubtful whether the pyrolysis of methane itself to furnish motor fuels will become commercially attractive.

The formation of aromatic hydrocarbons from methane is explained by Fischer and also by Stanley and Nash by the theory of nascent radicals. Wheeler and his collaborators, however, regard the olefin hydrocarbons, and especially ethylene, as the important intermediates in the formation of aromatics. The mechanism proposed by Wheeler involves the intermediate production of the free radical $:CH_2$, two of which combine to form ethylene. Polymerization of ethylene (a well-known thermal reaction) yields butylene which in turn loses hydrogen to form 1,3-butadiene. Wheeler concluded that butadiene then reacts with more ethylene according to the following scheme:



$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CH_2 \rightarrow \begin{cases} CH_2{=}CHCH_2CH_2CH{=}CH_2 \\ \text{or} \\ CH_2{=}CHCH{=}CHCH{=}CH_2 + H_2 \end{cases}$$

or



According to Hague and Wheeler,[26] ethylene fulfils all the requirements of a producer of benzene, and the theory proposed by these workers also takes into account the important rôle of diolefins, such as butadiene. Butadiene is always a product of high-temperature cracking and several prior workers, notably Davidson, arrived at the conclusion that this diolefin is a probable intermediate in the formation of aromatic hydrocarbons during pyrolysis.

The production of aromatic hydrocarbons from the homologues of methane is also easily explained on the basis of Wheeler's theory since lower olefins (especially ethylene) are always formed in quantity in the initial stages of decomposition. In the case of methane, however, some doubt has been cast on the general validity of the theory proposed by Wheeler, who appears to have ignored the considerable production of acetylene which takes place simultaneously with the formation of aromatic hydrocarbons. The formation of considerable amounts of acetylene in the region of 1050° to 1200° C. was noted by Stanley and Nash[27] and also by Frolich, White and Dayton.[28] The latter, as a result of their study of the formation of acetylene from methane by cracking under reduced pressure, concluded that acetylene is an intermediate in the production of benzene from methane. In the case of the higher paraffin hydrocarbons, which are converted into aromatics at a lower temperature than is methane, the intermediate production of acetylene is very doubtful. With the possible exception of methane, therefore, the theory of Wheeler regarding the mode of formation of aromatics during pyrolysis appears to fit the facts admirably.

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[26] *J.C.S.*, 1929, 378.
[27] *Loc. cit.*
[28] *Ind. Eng. Chem.*, 1930, 22, 20.

AROMATIC HYDROCARBONS FROM HOMOLOGUES OF METHANE

The fact that aromatic hydrocarbons may be obtained by pyrolysis of the homologues of methane has been known for some time. In 1916, Zanetti[29] subjected the propane-butane fraction of natural gas to pyrolysis in a silica tube at various temperatures, a Cottrell separator being employed to precipitate the tar fog. It was noted that the production of unsaturated gaseous hydrocarbons attained a maximum at about 750° C. Above this temperature the formation of aromatic hydrocarbons occurred and the proportion of unsaturated hydrocarbons decreased and became practically negligible at 1000° C. The curve of hydrogen formation was found to rise slowly with increasing temperature but more rapidly during the formation of aromatics. The principal gaseous unsaturated hydrocarbon was ethylene, but the presence of propylene was suspected. Butadiene was isolated as its tetrabromide, while benzene, toluene and naphthalene were shown to be present in the tar. Catalysts were used and it was observed that copper behaved in a manner similar to silica but nickel and iron induced a marked decomposition of the gas into its elements, the iron at 725° C. and the nickel at an even lower temperature, and no tar fog was produced in either case.

The pyrolysis of the ethane-propane fraction of natural gas was examined by Zanetti and Leslie.[30] As with the propane-butane fraction, the proportion of unsaturated hydrocarbons increased with increasing temperature to a maximum at about 750° C. and then decreased. As before, the beginning of the decrease in the proportion of unsaturated hydrocarbons and the rise in hydrogen production was coincident with the appearance of a tar fog and the formation of aromatic hydrocarbons. The tar obtained by the pyrolysis of ethane-propane mixtures above 750° C. was later examined by Zanetti and Egloff[31] and benzene, toluene, naphthalene and higher aromatics were identified.

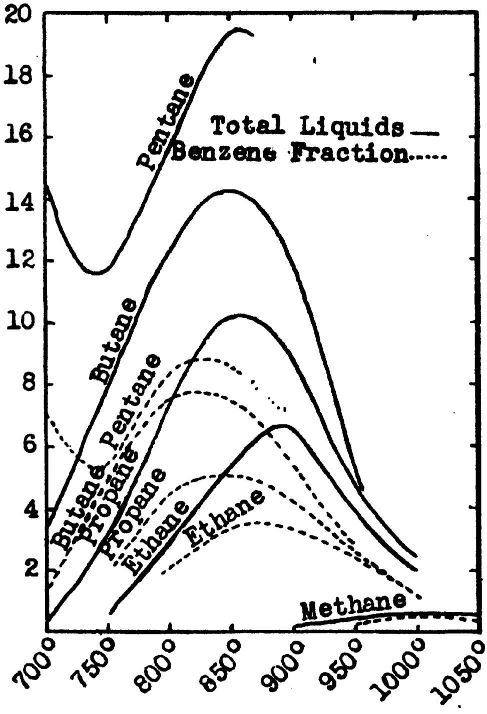
Further investigations of the formation of aromatic hydrocarbons by the pyrolysis of ethane-propane mixtures were carried out by Davidson,[32] who studied the effect of various catalysts on the progress of the decomposition. With the exception of iron, nickel and cobalt, metals do not seem to exert any great catalytic influence on the reaction nor do variations in the surface exposed appear to influence it. Iron, nickel and cobalt were found to be negative catalysts of the reaction yielding aromatic hydrocarbons, and they greatly accelerate the decomposition of the hydrocarbon gases into carbon and hydrogen. The optimum temperature for the production of aromatic hydrocarbons was found to be 850° C. Davidson further investigated the influence of pressure on the pyrolysis of ethane-propane mixtures. Up to 700° C. it was found that increasing the pressure increased the formation of unsaturated hydrocarbons and hydrogen. Above 700° C. increasing the pressure decreased the proportion of aromatic hydrocarbons. Davidson concluded from these pressure experiments that the main reaction resulting in the formation of aromatics from paraffin hydrocarbons begins at 700° C., and is accompanied by an increase in volume notwithstanding the fact that it is also a condensation reaction.

The formation of benzene and its homologues (and also of naphthalene and

[29] *Ind. Eng. Chem.*, 1916, **8**, 674.
[30] *Ind. Eng. Chem.*, 1916, **8**, 777.
[31] *Ind. Eng. Chem.*, 1917, **9**, 474.
[32] *Ind. Eng. Chem.*, 1918, **10**, 901.

other polynuclear aromatic compounds) from ethane at 700° to 900° C. was observed by Williams-Gardner.[33] He ascribed the formation of aromatic hydrocarbons to the peculiar behavior of ethylene (an intermediate product) in the region of 750° C.

A comprehensive study of the conversion of the lower paraffin hydrocarbons to aromatic hydrocarbons by pyrolysis was reported by Hague and Wheeler.[34] Perhaps the most striking feature of their results is the similarity they found



Courtesy Fuel.

FIG. 17.—Pyrolysis of Paraffin Hydrocarbons. Yields, at Various Temperatures, of Total Liquids and of Benzene in Grams per Gram-Mole of Hydrocarbon. (Hague and Wheeler.)

in the behavior of all the hydrocarbons studied, methane included, at the higher temperatures. Below 750° C. and in this temperature range each hydrocarbon follows an individual course. At higher temperatures secondary reactions take place which, however, yield the same type of products in all cases. The liquid products obtained by pyrolysis below about 750° C. contained appreciable proportions of unsaturated hydrocarbons and the light benzene fraction could not be solidified in a freezing mixture. When pyrolysis was effected at temperatures above 750° C. then nearly pure benzene could be separated by fractionation of the liquid tar. The yields of liquids and the temperature ranges over which such yields were obtained are shown in Figure 17 on the preceding page, in which the yields, expressed in grams per gram-mole, are plotted against the temperature. With increasing molecular weight from ethane to pentane the yields of liquids increase in the approximate ratio 2:3:4:5. The proportion of light distillate boiling from 80° to 90° C. was usually at a maximum at a temperature slightly below that for maximum yield of liquid and varied from 11.2 per cent by weight for ethane to about 19.0 per cent for n-hexane. The optimum yield of aromatic liquids (expressed in percentage by weight of the initial hydrocarbon) and the temperatures at which they were obtained are as follows:

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[33] *Fuel*, 1925, 4, 430.
[34] *Fuel*, 1929, 8, 512, 560.

Hydrocarbon	Temperature ° C.	Total Liquid % by Weight
Ethane	900	21.9
Propane	850	23.1
n-Butane	850	24.6
n-Pentane	850	26.8
n-Hexane	850	33.8

It should be noted that the homologues of methane give much higher yields of aromatic hydrocarbons on pyrolysis than methane itself. This point is emphasized by the results of some large-scale tests carried out by Dunstan[35] on the pyrolysis of two types of natural gas having the following percentage compositions:

Constituents	Gas I	Gas II
H_2S, O_2, and CO_2	1.6	9.7
N_2	1.4	1.7
CH_4	81.0	36.0
C_2H_6	16.0	32.0
C_3H_8	—	9.0
C_4H_{10}	—	9.0
C_6H_{12}	—	6.0

On the pyrolysis of these gases in silica tubes, gas I gave a yield of 220 gallons of benzene per 1,000,000 cubic feet, and gas II, 770 gallons of benzene and quantities of tar from the same volume of gas. It is evident, therefore, that gases comparatively rich in the homologues of methane give much higher yields of aromatic hydrocarbons than do "dry" gases consisting principally of methane itself.

The pyrolysis of ethane, propane and butanes (as well as mixtures of these) to produce aromatic oils has been the subject of an important study by Frey and Hepp,[36] who paid special attention to the time factor. The pyrolysis was carried out in silica reaction tubes heated electrically to the desired temperature, and the products of cracking were passed through an electric precipitator, where suspended tar was collected. The base of the tar precipitator was maintained at 60° C. to avoid condensation of toluene or lower-boiling components, and the gases issuing from it passed to a solid carbon dioxide-acetone bath to condense volatile liquid hydrocarbons. From the heats of formation of the reactants and the products, assuming a constant temperature of 850° C., variations in the heat content during cracking were calculated. In this manner Frey and Hepp were able to distinguish two well-defined thermal effects during the course of pyrolysis, namely, (1) a highly endothermic reaction corresponding to the formation of the maximum concentration of gaseous olefins and occurring at an exposure time of about 0.0025 minute, and (2) a marked exothermic reaction (about 190 calories per gram) corresponding to the aromatization of the gaseous olefins and developed at times of exposure of 0.0025 to 0.08 minute. In later experiments on a large scale these two distinct reactions were conducted separately. Butane was cracked at 750° to 770° C., under 2 atmospheres pressure, and then passed into an insulated chamber in which formation of aromatic hydrocarbons took place without the further introduction of heat. A temperature rise of over 50° C. was noted in the latter step. By sufficiently reducing the rate of flow (or increasing the time of contact) it was possible to obtain a temperature rise of more than 100° C.

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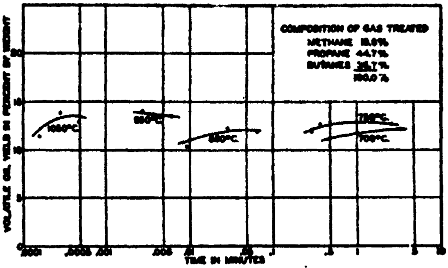
[35] *J. Roy. Soc. Arts,* 1928, 76, 922, 945, 985, 1001; *Chem. Abs.*, 1928, 22, 4235, 4781.

[36] *Ind. Eng. Chem.*, 1932, 24, 282. See also Gregory, U. S. Patent 1,847,241, Mar. 1, 1932; Guyer and Frey, U. S. Patent 1,847,242, Mar. 1, 1932; Oberfell, Guyer and Frey, U. S. Patent 1,847,259, Mar. 1, 1932; all patents assigned to Phillips Petroleum Co.; *Chem. Abs.*, 1932, 26, 2580. French Patent 733,134, 1932; *Chem. Abs.*, 1933, 27, 730.

The influence of time and temperature on the production of volatile aromatic oils was investigated by Frey and Hepp using, as a raw material, a gas consisting of 18.6 per cent methane, 44.7 per cent propane, and 36.7 per cent butanes. The yields of volatile oils obtained at temperatures varying from 700° C. to 1050° C. and at times of contact from about 0.0002 to 4 minutes are shown graphically in Figure 18. The remarkable fact is thus clearly demonstrated that, within this rather wide range of temperature, the maximum yield of volatile oils was approximately constant (being equal to about 14 per cent by weight of the gas mixture) for those limits of contact appropriate for each temperature. The minimum values of contact time required to develop a roughly maximum yield of oils within this temperature range were found to be related to the operating temperature by the empirical formula:



Courtesy Industrial and Engineering Chemistry.

FIG. 18.—Effect of Time and Temperature on Yields of Volatile Oils.
(Frey and Hepp.)

$$T = 690 - 100 \log t$$

where T = temperature in ° C.
and t = contact time in minutes

The effect of the time factor on the composition of the liquid and solid products of pyrolysis (at 850° C.) of the gas mixture mentioned above is shown in Table 40.

The volatile oils produced at shorter times of contact contained a large proportion of unsaturated hydrocarbons. The oil obtained in run 6, at the long contact time of 0.40 minute, consisted almost entirely of benzene.

To obtain more detailed information about the composition of the volatile oils, large quantities of these were prepared by Frey and Hepp by the pyrolysis

TABLE 40.—*Effect of Time Factor on the Composition of the Liquid and Solid Products of Pyrolysis.*

Run	1	2	3	4	5	6
Contact time, minutes	0.0025	0.006	0.010	0.042	0.08	0.40
Yields, % by weight						
Volatile oils	3.0	8.1	9.4	14.2	13.5	8.7
Tar	0.2	1.4	1.9	9.5	12.5	14.7
Carbon	0.03	0.13	0.10	0.60	1.3	11.5

(at 850° C. using different times of contact) of a gas mixture consisting of 89 per cent of n-butane and 11 per cent of isobutane. These oils were carefully examined by fractional distillation at temperatures below 15° C. in a modified column used for gas analysis. Propylene, butylene (mainly isobutylene) 1,3-butadiene, pentenes, cyclopentadiene, a hexene fraction consisting principally of hexadiene (and some methylcyclopentadiene), benzene, toluene, xylenes and styrene were found. From the results of these experiments (Table 41), it will be seen that in the early stages of benzene formation, butadiene, cyclopentadiene and other highly unsaturated hydrocarbons were present in fairly large proportions. As the time of contact is increased, however, the proportion of diolefins and of toluene decreases and benzene tends to become the main constituent of the volatile oils.

TABLE 41.—*Pyrolysis of 89% n-Butane and 11% Isobutane at 850° C.*

Run	1	2	3	4	5
Time of contact, minutes	0.0015	0.015	0.04	0.065	0.12
Yield, % by weight					
(1) Volatile oils	3	10.5	15.5	16.0	17.0
(2) Tar	0.0	5.0	9.5	11.0	17.0
Analysis of volatile oils, % by volume					
Propylene	—	?	0.9	0.7	1.9
Butenes	—	5	5	3	
Butadiene	—	4			
Pentenes	—	1	4	2.5	
Cyclopentadiene	—	6			
Hexadienes	—	1	0.3	0.5	
Benzene	—	61.1	74.8	82.8	92.0
Intermediate	—	0.9	1.0	1.0	0.3
Toluene	—	9.8	12.0	9.5	5.8
Intermediate	—	0.2	0.0	0.0	0.0
Xylenes, styrene	—	8	(2)	—	—

Experiments reported by Frey and Hepp on the pyrolysis of propane at a pressure of 9.5 atmospheres and a temperature of 750° C. indicated that the maximum yield of volatile oil under these conditions was about the same as that obtained at atmospheric pressure. Experiments in which different hydrocarbons were pyrolyzed under conditions giving a maximum yield of volatile oils showed that the yield of benzene and toluene increases with the carbon-hydrogen ratio in the initial hydrocarbon.

Thermal decomposition of isopentane at 680° C. in the presence of silica gel, at one atmosphere pressure and 15 seconds contact, yields about 75 per cent of gaseous and 25 per cent of liquid materials.[37] Methane, ethylene, propylene and butadiene were identified in the gases, and the liquids contained a large proportion of ethylenic and aromatic hydrocarbons.

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[37] Mailhe and Creusot, *Compt. rend.*, 1932, **194**, 2220; *Brit. Chem. Abs.* **A**, 1932, 830.

Podbielniak[88] has given an interesting account of large-scale experiments on the cracking of various mixtures of the lower paraffins to produce aromatic liquid hydrocarbons. At the high temperatures necessary for pyrolysis it was found that the heat-resistant alloy reaction tubes rapidly failed through oxidation on the outside and extensive carbonization on the inside. Because of the disadvantages connected with non-metallic refractories, special composition high-heat resistant alloys were subsequently used. The life of the tubes was increased by (1) careful control of the furnace temperature, (2) application of radiant heat rather than convection heat to the last alloy tube passing through the furnace, (3) careful regulation of the temperature gradient in the tubes, and (4) greatly increasing the gas velocity in the tubes. By taking these steps a material improvement in the effective life of the high-temperature reaction tubes was attained, and it was concluded that in a commercial plant the life of the reaction tubes should amount to many thousand hours at the high temperatures required for the maximum production of aromatics. Podbielniak also reported that at high gas velocities the formation and deposition of carbon on the tube walls was reduced to such an extent that the tube required blowing (with superheated steam or air) only about once every 8 to 12 hours. The carbon deposit was fairly light and fluffy and a blow period of only 15 minutes was usually sufficient to clean it out. At high gas velocities, the formation of hydrogen was suppressed to a very low figure.

The crude liquid obtained by pyrolysis contained 30 to 60 per cent of benzol, 15 to 20 per cent of toluol, and a residue consisting principally of higher aromatic hydrocarbons. The exact composition of the condensates depended upon the pyrolysis temperature and the times of contact but generally from 75 to 85 per cent of the product met motor fuel specifications for boiling range when distilled in an Engler apparatus.

Podbielniak also supplied data for the cracking of gaseous paraffin hydrocarbons particularly with respect to the production of ethylene. Table 42 summarizes some of the experimental results obtained in large-scale operations.

TABLE 42.—*Yield of Ethylene from Cracking of Gaseous Paraffin Hydrocarbons.*

Composition of Gas Cracked					Temperature Cracked Gas at Outlet ° F.	Total Gallons Aromatics per 1000 Cu. Ft. of Raw Gas	C_2H_4 in Cracked Gas Per Cent
CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5			
4.8	10.3	83.4	1.4	0.1	1500 1500	0.99 1.06	26.9 28.2
1.7	9.5	76.2	10.0	—	1550	—	26.8
2.1	10.0	76.2	11.5	0.2	1650 1740	1.6 2.7	10.9 —
16.4	4.0	61.2	18.3	0.1	1650	2.3	—
77.6	6.9	10.1	4.8	0.6	1650	0.5	—

Berl and Forst[89] reported that high molecular weight paraffin hydrocarbons, paraffin oil boiling (at 12 mm.) between 235° and 280° C. and paraffin wax (m.p. 68° C.), heated to 800° to 1000° C. in contact with porcelain yield aromatic

[88] *Oil and Gas J.*, 1931, 29 (52), 22; *Chem. Abs.*, 1931, 25, 5755.

[89] *Z. angew. Chem.*, 1931, 44, 833; *Chem. Abs.*, 1932, 26, 1234.

hydrocarbons. The latter consist largely of benzene, naphthalene and anthracene. Only a small proportion of aromatics having side chains were formed.

MECHANISM OF THE FORMATION OF AROMATIC HYDROCARBONS FROM METHANE HOMOLOGUES

It is now generally agreed that aromatic hydrocarbons are not the primary results of the pyrolysis of the lower paraffin hydrocarbons but are formed by secondary changes induced by the further action of heat on the primary decomposition products. Three principal theories of aromatic formation have been proposed. Berthelot's[40] theory assumes the intermediate to be acetylene which undergoes direct polymerization to aromatic hydrocarbons. However all the evidence of later experimental work indicates that acetylene is formed only to a very slight extent in the temperature range yielding aromatic hydrocarbons most readily. Nevertheless with methane, which required much higher temperatures than its homologues for conversion into aromatic hydrocarbons, the intermediate formation of acetylene is a distinct possibility.

A second theory[41] involves the intermediate production of a cyclohexane which loses hydrogen to become an aromatic hydrocarbon. The cycloparaffin intermediate might be derived from a paraffin in one of three ways, namely (1) by simple ring closure of an olefin of six or more carbon atoms which originates from a paraffin of the same or larger number of carbon atoms by splitting; (2) by the polymerization of an olefin with ring closure; or (3) by the intermediate formation of free radicals, such as $:CH_2$, followed by polymerization.

According to the third theory, which appears to be substantiated by experimental evidence to a greater extent than either of the others, the intermediate substances responsible for the formation of aromatic hydrocarbons are the monolefins and the diolefins, particularly butadiene. The exact details of this mechanism are yet subjects of disagreement.

Davidson[42] was apparently the first investigator to emphasize the probable importance of butadiene as an immediate precursor of aromatics. Wheeler and Hague,[43] as previously noted, suggested that benzene is produced by the direct combination of butadiene with ethylene. Butadiene is the result of the dehydrogenation of butylene, which may be formed either by the splitting of a higher paraffin or by the polymerization of ethylene molecules. Later Wheeler and Wood[44] adduced evidence to show that ethylene and butadiene combine in equimolecular proportions to produce cyclohexene, and that similar condensations of propylene or butylene with butadiene yield substituted hydroaromatic hydrocarbons. The latter rapidly lose hydrogen at the high temperatures of pyrolysis to give benzene and its homologues.

A very careful investigation of this question has been carried out by Schneider and Frolich,[45] who made a study of the initial products of the pyrolysis of propane, propylene, ethylene, and butadiene at temperatures above 700° C. with very short times of contact, i.e., low percentage cracking. According to these investigators, butadiene appears to be formed directly from ethylene, without the intermediate formation of butylene, by the reaction

$$2C_2H_4 \longrightarrow C_4H_6 + H_2$$

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[40] *Compt. rend.*, 1866, **62**, 905; 1867, **63**, 788, 834.

[41] Ipatiev, *Ber.*, 1911, **44**, 2978; Ipatiev and Dovgelevitsch, *ibid.*, 1911, **44**, 2987; Ipatiev and Rutala, *ibid.*, 1913, **46**, 1748; *cf.* Hurd and Spence, *J.A.C.S.*, 1929, **51**, 3561.

[42] *Ind. Eng. Chem.*, 1918, **10**, 901.

[43] *J.C.S.*, 1929, 378.

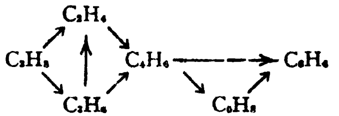
[44] *J.C.S.*, 1930, 1819.

[45] *Ind. Eng. Chem.*, 1931, **23**, 1405.

Experiments on the pyrolysis of a mixture of ethylene (90 per cent) and butadiene (10 per cent) at 725° C. and 0.2 atmosphere pressure showed clearly that the two principal primary reactions may be represented thus:

$$C_4H_6 + C_2H_4 \longrightarrow C_6H_8 + H_2$$
$$C_4H_6 + C_2H_4 \longrightarrow C_6H_6 + 2H_2$$

The data suggest that part of the benzene is formed directly while part of it originates by dehydrogenation of the intermediately formed triolefin, C_6H_8. The work of Schneider and Frolich is therefore consistent with the view of others that benzene is produced in pyrolytic processes by a combination of ethylene with butadiene either directly or through an intermediate triolefin. The reaction scheme by which another typical lower paraffin, propane, is converted into benzene is as follows:



Just as butadiene reacts with ethylene to yield benzene, so benzene undergoes further reaction to yield alkylated derivatives, naphthalene, and eventually tarry compounds of high molecular weight.

AROMATIC HYDROCARBONS FROM ETHYLENE

A number of investigators have shown clearly the possibility of producing aromatic hydrocarbons from ethylene by pyrolysis. The important function assigned to ethylene by Hague and Wheeler as an intermediate in the formation of aromatics by the thermal decomposition of paraffin hydrocarbons has already been mentioned. Ethylene appears to be fairly stable up to about 700° to 750° C. Above this temperature there is a marked tendency for this olefin to form aromatic hydrocarbons. Hague and Wheeler found that the optimum temperature for the production of liquid hydrocarbons (mainly benzene) from ethylene in the presence of silica or porcelain surfaces is 750° to 800° C. The total yield of liquid, at 800° C., represented 28.9 per cent of the ethylene passed. Dilution of the ethylene with hydrogen decreased the yield of benzene and the temperature of maximum yield was increased. The formation of liquid hydrocarbons by the non-catalytic thermal decomposition of ethylene at atmospheric or increased pressures has been investigated by Waterman and Tulleners.[46] Appreciable yields of aromatic hydrocarbons have been obtained by Mailhe and Renaudie[47] by passing ethylene over a mass of silica gel granules heated to 700° C. In addition to benzene and toluene, unsaturated hydrocarbons were present in the light fractions.

Berl and Forst[48] procured yields as high as 43 per cent of liquid products from ethylene by circulating this gas for several hours through a porcelain tube heated to 800° to 900° C. The ratio of light oils to heavy oils in the liquid condensate, which was principally aromatic, was dependent upon the temperature and the velocity of circulation. The liquids contained benzene, naphthalene, anthracene and their homologues together with a small proportion of cyclo-

[46] *Brennstoff-Chem.*, 1930, 11, 337. *J. Inst. Pet. Tech.*, 1931, 17, 506.

[47] *Compt. rend.*, 1930, 191, 265. This work on the transformation of gaseous hydrocarbons into liquid fuels is reviewed by Mailhe (*Tech. moderne*, 1931, 23, 581, 621; *Chem. Abs.*, 1932, 26, 279).

[48] *Z. angew. Chem.*, 1931, 44, 193; *Brit. Chem. Abs.* A, 1931, 596.

pentadiene. Packing the tube with pieces of porcelain slightly increased the total yield as well as the proportion of light oil. The presence of metals, or metallic oxides, greatly reduced the formation of liquid products, presumably because of the activity of these substances in catalyzing the decomposition of ethylene into its elements.

The important influence of pressure in promoting the conversion of ethylene into liquid hydrocarbons is well known from the work of Ipatiev and others.[49] Under pressures of about 70 atmospheres, and higher, a rapid conversion of ethylene into liquid hydrocarbons (not aromatic, but principally paraffins and cycloparaffins) occurs even at temperatures as low as 350° C. Most of the work on the conversion of ethylene and its homologues into aromatic hydrocarbons has been done at temperatures of 600° C. and above and at atmospheric pressure. Increased pressure accelerates the conversion to liquid hydrocarbons, but at the same time it suppresses the formation of aromatics. Thus Frolich,[50] from his experiments with ethylene and propylene, showed that when the pressure is increased and the temperature of pyrolysis maintained constant, the proportion of hydrogen liberated becomes less and the liquid products lose more of their aromatic character until, at pressures of several thousand pounds per square inch, the liquid material obtained is decidedly non-aromatic even when the reaction temperature is as high as 600° C. The heat treatment of olefin gases under pressure to yield liquid hydrocarbons of a non-aromatic character has been investigated also by Dunstan, Hague and Wheeler.[51]

AROMATIC HYDROCARBONS FROM HOMOLOGUES OF ETHYLENE

The homologues of ethylene are similarly converted into a mixture of aromatic hydrocarbons when subjected to pyrolysis at temperatures of 600° C. and higher at atmospheric pressure. As with ethylene, the application of higher pressures tends to favor condensation to non-benzenoid liquid hydrocarbons, even at temperatures as high as 600° C. The most comprehensive investigations of the pyrolysis of the immediate homologues of ethylene are those of Wheeler and Wood [52] and Hurd and his collaborators.[53]

The yields of liquid products obtained by Wheeler and Wood in the pyrolysis of propylene in a vertical quartz tube, at atmospheric pressure and at temperatures varying from 650° to 900° C., are shown in Table 43. Analyses of the resulting gases have already been given in Table 19.

TABLE 43.—*Pyrolysis of Propylene.*

		Yields (Per Cent by Weight of Propylene Treated)		
Temp. ° C.	Contact Time Secs.	Total Liquids	Distillate up to 170° C.	Carbon
650°	58.2	5.2	3.2	Nil
700°	55	20.3	12.9	Trace
750°	52.5	35.6	20.4	Trace
800°	50	40.6	19.0	1.7
850°	47.7	33.8	14.6	9.5
900°	45.7	11.9	6.8	—

[49] A review of this work is given in Chapter 2 and is discussed further in Chapter 26.
[50] *Chem. Met. Eng.*, 1931, 38, 343; see also Frolich and Wiezevich, *Ind. Eng. Chem.*, 1932, 24, 13.
[51] *J.S.C.I.*, 1932, 131T.
[52] *J.C.S.*, 1930, 1819.
[53] Hurd and Meinert, *J.A.C.S.*, 1930, 52, 4978. Hurd and Spence, *J.A.C.S.*, 1929, 51, 3561.

The liquids of lower boiling point, obtained at 650° C., were said to be mainly unsaturated monocyclic paraffins of the cyclohexene type, while those produced at 700° C. and higher were principally benzene and toluene. The proportions of benzene and toluene formed from propylene at 700° C. were greater than from ethylene under similar conditions.

Hurd and Meinert obtained yields of aromatic liquids, amounting to 20 to 25 per cent by weight of the propylene decomposed, by pyrolysis in pyrex or quartz tubes at 700° C. and higher. Mailhe and Renaudie[54] conducted propylene over a silica gel contact mass at 650° C. and produced a liquid condensate containing low-boiling olefins together with aromatic hydrocarbons and a tar in which toluene, m-xylene, naphthalene and anthracene were detected.

By the pyrolysis of both 1-butene and 2-butene in quartz tubes at temperatures ranging from 600° to 900° C., Wood and Wheeler secured yields of aromatic liquids as high as 40 per cent by weight of the butene employed. Table 44 summarizes the results of these investigators. Gas analyses are shown in Table 20.

Table 44.—*Pyrolysis of 1-Butene and 2-Butene.*

		Yields (Per Cent by Weight of Butene Treated)					
		From 1-Butene			From 2-Butene		
Temp. ° C.	Contact Time Secs.	Total Liquids	Distillate up to 170° C.	Carbon	Total Liquids	Distillate up to 170° C.	Carbon
600°	61.5	12.9	6.5	Nil	5.2	1.4	Nil
650°	58.2	29.8	20.3	Nil	27.0	17.2	Nil
700°	55	35.8	23.6	Trace	37.0	25.8	Trace
750°	52.5	39.6	22.4	Trace	39.6	23.2	Trace
800°	50	39.4	19.9	1.0	37.9	18.6	1.4
850°	47.7	35.0	16.2	4.7	31.6	14.2	4.7
900°	45.7	13.9	7.8	7.1	12.4	6.1	5.4

In the liquid products obtained by the decomposition of a mixture of 1-butene and 2-butene, at 600° C., cyclohexene and methylcyclohexene predominated; cyclohexadiene and methylcyclohexadiene were also present; and benzene and toluene were found only in comparatively small proportions. Only 18.5 per cent of this liquid product boiled above 117° C. On the other hand, of the liquids formed from pure 2-butene at 650° C., 29.6 per cent boiled above 110° C. and 16.6 per cent above 150° C., both fractions consisting largely of aromatic hydrocarbons.

The pyrolysis of isobutene was studied by Hurd and Spence,[55] who found that at 700° C. and a contact time of 18 seconds the yield of liquid products was about 30 per cent by weight of the isobutane used or about 63 per cent of the isobutane decomposed. By fractional distillation about one-half of this condensate was shown to be benzene and toluene. The remainder appeared to be a mixture of xylenes, naphthalene, methylnaphthalene, diphenyl, ditolyl (?), anthracene, phenanthrene, and other aromatic hydrocarbons.

Mailhe and Renaudie[56] reported the conversion of 1-butene and 2-butene into liquid hydrocarbons by passage over a contact mass of silica gel at 650° to 700° C.

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[54] *Compt. rend.*, 1930, **191**, 851; *Brit. Chem. Abs.* **A**, 1931, 60.
[55] *Loc. cit.*
[56] *Compt. rend.*, 1931, **192**, 561; *Brit. Chem. Abs.* **A**, 1931, 460.

From 1-butene, at a temperature 650° to 670° C., a yield of 33 per cent (by weight of the butene charged per single passage) of liquid hydrocarbons was obtained, and also methane and propylene. The liquid contained benzene, toluene, and m-xylene, totaling about 21 per cent, but neither naphthalene nor anthracene. Under the same conditions similar results were obtained with isobutylene. By heating 2-butene to 700° C. in the presence of silica gel, the yield of liquids, consisting largely of aromatic hydrocarbons, was 37.7 per cent of the weight of the butene charged. This butene differed from the other two in that it produced a tar in which both naphthalene and anthracene were found.

Ivanov [56a] found that the liquid product obtained by pyrolysis of an ethylene concentrate from cracked mineral oil consisted chiefly of benzene and olefin hydrocarbons. The gas was passed through a silica tube at 550°-580° C. under a pressure of 1 atmosphere. On raising the temperature the benzene content increased while the olefin content decreased. In the presence of zinc chloride at a temperature of 320°-360° C. and a pressure of 30 to 70 atmospheres, a maximum yield of low-boiling products was obtained which consisted of paraffin, olefin, aromatic and naphthene hydrocarbons.

AROMATIC HYDROCARBONS FROM ACETYLENE

The fact that acetylene can be converted into aromatic hydrocarbons by thermal treatment has long been known and indeed constitutes a classical synthesis of benzene and its homologues. The most favorable temperatures for conversion appear to lie within the range of 600° to 700° C. Above the higher temperature the condensation reaction is largely replaced by decomposition of acetylene to carbon and hydrogen, accompanied by hydrogenation to ethylene, ethane and methane. Extensive work on the formation of aromatic hydrocarbons from acetylene was carried out by Meyer and his collaborators,[57] who identified the following hydrocarbons among the products of pyrolysis: hexane, benzene, toluene, o-, m-, and p-xylenes, styrene, pseudocumene, mesitylene, indene, naphthalene, methylnaphthalenes, diphenyl, acenaphthene, fluorene, anthracene, pyrene, phenanthrene, fluoranthrene and chrysene.

The condensation of acetylene to liquid hydrocarbons has been investigated by Fischer, Bangert and Pichler,[58] who passed the gas over active charcoal at 600° to 700° C. Hydrogen, methane and carbon were among the products formed, and the carbon, thus liberated, appeared to be an effective catalyst for the condensation reactions. About 70 per cent of the acetylene was converted into light and heavy oils in approximately equal proportions. The light oil contained 70 per cent aromatic hydrocarbons and 30 per cent unsaturated hydrocarbons. The addition of carbon dioxide to the acetylene increased the proportion of light oil and assisted in regenerating the catalyst.

Berl and Hofmann [59] obtained a yield of 98 per cent of liquid products by the pyrolysis of acetylene. An electrically heated copper block, which permitted the maintenance of a constant temperature, was used as a furnace. By placing this furnace in a vertical position the liquid reaction products could be easily withdrawn. Iron, silica, tin or calcium oxides were found to be unfavorable to the conversion. Good yields of aromatic hydrocarbons were, however, obtained with carbon as a contact agent at temperatures between 600° and 700° C.

[56a] *J. Applied Chem. Russ.*, 1933, 6, 103; *Brit. Chem. Abs.* B, 1933, 612.

[57] Meyer, *Ber.*, 1912, 45, 1609; Meyer and Tanzen, *ibid.*, 1913, 46, 3183; Meyer and Fricke, *ibid.*, 1914, 47, 2765; Meyer and Wesche, *ibid.*, 1917, 50, 422; Meyer and Meyer, *ibid.*, 1918, 51, 1571.

[58] *Brennstoff-Chem.*, 1929, 10, 279.

[59] *Z. angew. Chem.*, 1931, 44, 259. *Cf.* Ylla-Conte, Swiss Patent 143,697, 1928; *Chem. Abs.*, 1931, 25, 4010.

The condensation of three molecules of acetylene to one molecule of benzene is an exothermic reaction. The heat thus liberated must be kept from the reacting gas and this, Berl and Hofmann reported, can be accomplished by mixing carbon dioxide with the acetylene. Carbon dioxide not only has a high specific heat but it is capable, as Fischer and his collaborators[60] have shown, of burning off carbon deposits in the furnace. Berl and Hofmann further observed that the addition of water vapor to the gases distinctly improved the polymerization of acetylene.

The importance assigned by earlier investigators to acetylene as an intermediate in the formation of aromatic hydrocarbons during pyrolytic reactions has been disproved by later work. It is almost certain that (with the possible exception of methane) the formation of aromatics by the pyrolysis of gaseous hydrocarbons takes place through the intermediate production of olefins and diolefins rather than of acetylene.

AROMATIC HYDROCARBONS FROM CYCLOPARAFFINS

Of the non-aromatic cyclic hydrocarbons, cyclohexane and its homologues appear to be most readily converted directly into benzene derivatives by heat in the presence of catalysts. Zelinsky and his co-workers[61] ascertained that the dehydrogenation of cyclohexane to benzene is a reversible reaction under certain conditions. In the presence of palladium or platinum black, benzene is readily hydrogenated to cyclohexane at 100° to 110° C., and at higher temperatures (the maximum being 300° C.) the dehydrogenation of cyclohexane to benzene predominates. Zelinsky also made the important discovery that palladium or platinum black are selective catalysts for the dehydrogenation of cyclohexane hydrocarbons but do not affect other cycloparaffin rings. For example, menthane and hexahydroxylenes can be dehydrogenated over platinum black at 300° to 310° C. to yield the corresponding aromatic hydrocarbons, cymene and the xylenes.[62] Certain cyclohexane homologues are, however, resistant to this dehydrogenation and Zelinsky[63] found that 1,1-dimethylcyclohexane was unchanged by passage over the platinum catalyst at 300° C.

The dehydrogenation of cyclohexane hydrocarbons to aromatics can be accomplished also in the presence of catalysts other than platinum or palladium, but side reactions involving the fission of C—C bonds occur at the same time. Sabatier and Senderens[64] reported that cyclohexane and some of its homologues are partly converted into aromatic hydrocarbons in the presence of nickel at about 280° C., methane and hydrogen being simultaneously formed. According to Zelinsky and Kommarewsky,[65] cyclohexane can be dehydrogenated to benzene and methylcyclohexane to toluene in the presence of nickel deposited on alumina at 300° to 310° C. without the formation of methane and other byproducts. Copper has also been suggested as a dehydrogenating catalyst for the conversion of cyclohexane hydrocarbons to benzene derivatives, but a much higher temperature (550° C.) appears to be required and carbon-to-carbon scission occurs with the simultaneous appearance of ethylene, propylene and butadiene.

The non-catalytic pyrolysis of cyclohexane and its homologues yields aromatic hydrocarbons but at the same time extensive carbon-to-carbon scission takes place forming methane, ethylene, ethane and butadiene.[66]

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[60] *Loc. cit.*

[61] *Ber.*, 1911, **44**, 3121; 1912, **45**, 3679. For equilibrium constants of the reaction, $C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$, see Zharkova and Frost, *J. Gen. Chem.* (*U.S.S.R.*), 1932, **2**, 534; *Chem. Abs.*, 1933, **27**, 888; also Purdum and Pease, *J.A.C.S.*, 1933, **55**, 3109.

[62] *Ber.*, 1923, **56**, 787.

[63] *Ber.*, 1923, **56**, 1716. See also Zelinsky and Kanzansky, *Ber.*, 1931, **64**, 2265.

[64] *Ann. chim. phys.*, 1905, (8) **4**, 363, 457; *Compt. rend.*, 1897, **124**, 616.

[65] *Ber.*, 1924, **57**, 667.

The dehydrogenation of naphthenes, or of petroleum fractions rich in them, is accomplished in the presence of certain catalysts containing cobalt or iron. An example of such a catalyst is one prepared by depositing a mixture of ammonium tungstate, cobalt nitrate and antimonic acid on active carbon and subjecting the mass to a stream of hydrogen sulphide at 350° C. for four hours.[67]

The cycloparaffins which do not contain rings of six carbon atoms apparently do not decompose directly into aromatic substances but isomerize first to straight-chain olefins. Secondary reactions at high temperatures (750° C.) undoubtedly convert the latter partly into aromatic hydrocarbons.

TECHNICAL PROCESSES

The most prominent feature in the technical development of the synthesis of aromatic hydrocarbons is the increasing attention directed toward the utilization of methane and its immediate homologues in natural gas as raw materials. Thus for example, Goudet[68] described a procedure for obtaining higher hydrocarbons from methane by heating this gas to 500° to 590° C., cooling suddenly to 250° to 350° C., and then submitting the gaseous product to the action of catalysts. The whole sequence of operations is conducted under high pressure.

In a process developed by the I. G. Farbenindustrie A.-G., methane, or gases containing methane, is passed over catalysts, such as the carbonates of the alkaline metals or the oxides or carbonates of magnesium or beryllium, at temperatures varying from 500° C. to 800° C. The reaction is carried out under pressure, which may be as high as 1000 atmospheres.[69] These same catalysts can be used, without the application of pressure, with the gases (containing both saturated and unsaturated, especially olefinic, hydrocarbons) from the low-temperature carbonization of carbonaceous materials.[70]

Another procedure for converting methane, or its gaseous homologues, into aromatic hydrocarbons consists of heating in two stages, first at temperatures of about 500° C., and subsequently as high as 950° C. Liquid hydrocarbons are separated after each stage. The reaction is carried out in tubes which may contain catalysts, such as silicon or graphite, with heating periods of 10 to 60 seconds.[71]

In addition to graphite and silicon, which may be used in the free or elemental state molded into bricks bonded with clay, alumina or water glass,[72] many other catalysts have been suggested. Examples are: firebricks or silicon bricks impregnated with copper salts, or refractory materials such as alloys of chromium and nickel, ferro-silicon, or silicon carbide[73]; oxides of chromium, tungsten, vanadium, or uranium, or mixtures of them[74]; chromium, tungsten, molybdenum, or alloys of these metals.[75] The last named are resistant to high temperatures and do not promote deposition of carbon. The elements selenium, tellurium and thallium, or their compounds, have also been proposed.[75a] The pyrolysis of gaseous paraffinic or olefinic hydrocarbons (at temperatures of 400° to 1100° C.) in the presence of the vapors of metals melting below 500° C. (the alkali metals excepted) has been described.[76] In general, catalysts for the conversion of gaseous paraffin hydrocarbons into aromatics may also be used for similar pyrolytic reactions with gaseous olefins. Aromatic hydrocarbons are made by passing methane, or other paraffin hydrocarbons, through heated non-metallic refractory chambers (Chamotte or silicon carbide) having the inside walls coated with a glaze of a silicate, phosphate, or borate of an alkali or alkaline-earth metal, or of copper, manganese, lead or chromium.[77] These catalysts are also said to prevent carbon formation.

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[66] Jones, *J.C.S.*, 1915, **107**, 1582. Frolich, Simard and White, *Ind. Eng. Chem.*, 1930, **22**, 240.

[67] I. G. Farbenindustrie A.-G., French Patent 688,369, 1930; *Chem. Abs.*, 1931, **25**, 709.

[68] British Patent 255,493, 1926; assigned to H. Spindler; *Brit. Chem. Abs.* **B**, 1927, 868.

[69] British Patent 258,608, 1926; *Brit. Chem. Abs.* **B**, 1928, 255. Pier, Pungs and Wietzel, U. S. Patent 1,851,726, Mar. 29, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2987.

[70] I. G. Farbenindustrie A.-G., British Patent 311,899, 1928; *Brit. Chem. Abs.* **B**, 1929, 589.

[71] I. G. Farbenindustrie A.-G., British Patent 361,944, 1931; *Brit. Chem. Abs.* **B**, 1932, 137; French Patent 717,494, 1931; *Chem. Abs.*, 1932, **26**, 2747. French Patent 708,810, 1931; *Chem. Abs.*, 1932, **26**, 993. Winkler, Haeuber and Feiler, U. S. Patent 1,922,918, Aug. 15, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 5082.

[72] I. G. Farbenindustrie A.-G., British Patent 357,170, 1930; *Chem. Abs.*, 1932, **26**, 5572; British Patent 363,344, 1930; *Chem. Abs.*, 1933, **27**, 1638.

[73] I. G. Farbenindustrie A.-G., British Patent 337,434, 1929; *Brit. Chem. Abs.* **B**, 1931, 194; British Patent 376,397, 1931; *Brit. Chem. Abs.* **B**, 1932, 926. Steigerwald, U. S. Patent 1,905,520, Apr. 25, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3481.

[74] I. G. Farbenindustrie A.-G., British Patent 366,107, 1930; *Brit. Chem. Abs.* **B**, 1932, 493; French Patent 717,412, 1931; *Chem. Abs.*, 1932, **26**, 2748.

Dunstan and Wheeler[78] reported the production of aromatics when a stream of gas, containing paraffins, is first gradually heated to a temperature (e.g., 550° C.) substantially below that required for decomposition, and then to a temperature (650° to 975° C.) at which the paraffins are decomposed and aromatics formed. Afterward the gas stream is expanded, cooled, and its velocity reduced, thus allowing deposition of the free carbon formed. The aromatic hydrocarbons are condensed and separated. If necessary the original gas is previously freed from hydrogen sulphide and condensible hydrocarbon vapors. The yield of aromatic hydrocarbons is said to be increased by dilution with an inert gas (steam) which is best introduced into the gas stream between the preheater and the reaction tubes. The reaction temperature is controlled at a point depending upon the paraffin or mixture of paraffins present. The suggested temperature ranges are 850°-975° C., 800°-900° C., 750°-800° C., 700°-800° C., and 650°-750° C., for methane, ethane, propane, butane; and pentane, respectively. For mixtures, a range of temperature is chosen suitable to the proportions of the constituents. The velocity of the gas in the preheater tubes and reaction tubes is so maintained that the flow is turbulent, giving good heat-transfer and maintaining the carbon particles in suspension. The residual gas, after the separation of free carbon and liquid aromatic hydrocarbons, may be utilized for the production of carbon black by combustion with a restricted supply of air, or it may be converted to oxygenated organic compounds such as alcohols, aldehydes or acids, particularly when it contains carbon monoxide or after the addition of that gas.[79]

Dunstan and Hague[79a] later employed a two-stage treatment for the production of aromatic compounds. In the first stage, the heating is conducted at 650°-800° C. under atmospheric pressure, which converts the paraffin hydrocarbons into olefins. In the second, the olefins are polymerized and condensed by heating at 350°-550° C. under pressures of 200 to 2000 pounds per square inch. To minimize the production of carbon, the apparatus is constructed of or lined with copper, aluminum or stainless steel.

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[75] I. G. Farbenindustrie A.-G., British Patent 366,494, 1930; *Chem. Abs.*, 1933, **27**, 1889; French Patent 711,331, 1931; *Chem. Abs.*, 1932, **26**, 1615.

[75a] I. G. Farbenindustrie A.-G., German Patent 547,080, 1924; *Chem. Abs.*, 1932, **26**, 3513; German Patent 545,164, 1924; *Chem. Abs.*, 1933, **26**, 2987; German Patent 564,404, 1925; *Chem. Abs.*, 1933, **27**, 991; all patents additions to German Patent 509,406, 1924; *Chem. Abs.*, 1931, **25**, 709.

[76] I. G. Farbenindustrie A.-G., British Patent 366,112, 1930; *Brit. Chem. Abs.* **B**, 1933, 330.

[77] I. G. Farbenindustrie A.-G., British Patent 368,257, 1930; *Chem. Abs.*, 1933, **27**, 2157.

[78] British Patent 309,455, 1927; *Brit. Chem. Abs.* **B**, 1929, 509; British Patent 377,716, 1931; *Brit. Chem. Abs.* **B**, 1932, 926; French Patent 658,348, 1928; *Chem. Abs.*, 1929, **23**, 5193. *Cf.* Coxon, British Patent 374,017, 1932; *Chem. Abs.*, 1933, **27**, 3942. All patents assigned to Anglo-Persian Oil Co., Ltd.

[79] Dunstan and Wheeler, British Patent 327,715, 1928; assigned to Anglo-Persian Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1930, 650.

[79a] British Patent 385,981, 1931; assigned to Anglo-Persian Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1933, 258.

In the process of Fischer and Pichler[80] methane, pure or diluted with other gases, is converted into benzene and other aromatic hydrocarbons by subjecting it to a temperature of 1000° to 1100° C. for a period of time not exceeding 1 second (best $\frac{1}{6}$ to $\frac{1}{20}$ second) in the absence of catalysts or oxygen-containing gases. Reaction is secured by passing the gas at a high velocity through narrow tubes maintained at the required temperature. Some free hydrogen, produced at the same time, may be reconverted to methane, e.g., by reaction with carbon monoxide in the presence of a catalyst, and the methane converted into additional aromatic hydrocarbons. Later Fischer[81] described an apparatus for this process consisting of a tower lined with silica and heated by furnace gases to the desired temperature. When sufficiently hot, a reverse (downward) current of methane is substituted, the products being removed from the base of the tower. As soon as the methane conversion falls off furnace gases are again led in, and the cycle is repeated as often as desired. A heat exchanger is arranged to preheat the methane and combustion gases alternately.

Lewis[82] described a procedure for the pyrolysis of natural gas in which about 90 per cent of the gas is conducted through tubes heated by the combustion of the other 10 per cent. The gases formed during the heat treatment are mixed with the hot products of combustion and the mixture is expanded, cooled, and passed through an absorber for the removal of benzene. The residual gases may be burned to yield carbon black and the waste heat utilized in preheating the raw gas.

According to Youker,[83] liquid hydrocarbons are obtained by heating natural gas at temperatures above 750° C. under pressures greater than 500 pounds per square inch.

Snelling[83a] heated gaseous hydrocarbons at 400° to 649° C. under a pressure of 800 to 3000 pounds per square inch and returned a portion of the uncondensed gas to the reaction zone for further treatment. The liquid products were separated by condensation under a lower pressure.

Either aromatic or olefinic hydrocarbons may be produced by the pyrolysis of mixtures of gaseous hydrocarbons (both saturated and unsaturated) at temperatures of 1000° to 1200° C. and at space velocities of 50 to 100 reciprocal minutes or more. For high yields of aromatic hydrocarbons lower space velocities are required and at higher space velocities olefins or diolefins are formed. The reactions may be carried out in two or more stages with the removal of light oils or olefinic hydrocarbons after each stage. Also each stage is effected at a higher temperature or a lower space velocity than the preceding one. The reaction chambers, which should be very narrow in relation to their other dimensions, may be made of carborundum, graphite or heat-resisting alloys. If the walls are coated with alumino-silicate refractories, such as sillimanite, an increased proportion of naphthalene is obtained. The intermediate products of pyrolysis include propylene, ethylene and acetylene, and the final ones are light oils, methane, hydrogen and carbon. For example, a gaseous mixture consisting of 45 per cent methane, 24 per cent ethane, 21 per cent propane, and 10 per cent butane gave 0.32 gallon of light oil per 1000 cubic feet in a one-stage treatment, and 1.08 gallons in a three-stage treatment.[84]

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[80] British Patent 316,126,1928; *Chem. Abs.*, 1930, **24**, 1649; French Patent 686,040, 1928; *Chem. Abs.*, 1930, **24**, 5764.

[81] British Patent 319,340, 1928; *Brit. Chem. Abs.* **B**, 1930, 408.

[82] U. S. Patent 1,854,205, April 19, 1932; *Chem. Abs.*, 1932, **26**, 3364; British Patent 316,999, 1929; *Brit. Chem. Abs.* **B**. 1930, 937.

[83] U. S. Patent 1,800,586, April 14, 1931; *Chem. Abs.*, 1931, **25**, 3467.

[83a] U. S. Patent 1,880,189, Oct. 27, 1932; assigned to Gasoline Products Co., Inc.; *Brit. Chem. Abs.* **B**, 1933, 852.

An apparatus for the conversion of methane into aromatic liquid hydrocarbons, described by Otto,[85] consists of a modified coke-oven setting, in which the gas is passed through channels in the brickwork or in which the ovens themselves are used as contact chambers. The necessary heat is provided by the combustion of gas in an adjoining chamber, with heat exchangers between the ingoing and outgoing gases to increase the economy of the system. A temperature range of 1040° to 1060° C. yields the best results with pure methane.

Wheeler and Fletcher[86] developed an apparatus for carrying out endothermic gas reactions, such as the pyrolysis of gaseous hydrocarbons to produce aromatic liquids, at temperatures above 1000° C. and at high space velocities. It consists of a series of unpacked reaction chambers which are long, deep, and very narrow and are placed between long, deep heating-flues. The width of these chambers is about one-half inch and they are made of refractory material. After the desired reactions have taken place the products are passed through heat exchangers for preheating the incoming gaseous reactants.

In the process of Wheeler and Francis[87] the pyrolysis of hydrocarbon gases to liquid hydrocarbons is combined with the production of carbon bisulphide without seriously affecting the yields of aromatic hydrocarbons normally obtained. The gaseous hydrocarbons are mixed with sulphur vapor and the mixture passed through a heated reaction zone at a high temperature and a high space velocity. Instead of sulphur vapor, substances which yield sulphur at high temperatures (e.g., hydrogen sulphide) may be substituted. The apparatus of Wheeler and Fletcher can be used for this purpose, and all of the sulphur is said to be converted into carbon bisulphide.

According to Bampfylde,[88] reaction chambers for the pyrolysis of hydrocarbons may be constructed of, or surfaced with, a special iron alloy containing 10 to 16 per cent of aluminum and as much as 6 per cent chromium. Such alloys are particularly useful in the treatment of gaseous paraffinic or olefinic hydrocarbons at 550° to 1250° C. to yield aromatic hydrocarbons, and in the formation of liquid polymers from gaseous olefins at 350° to 500° C. under elevated pressures.

The conversion of methane, or a gas rich in methane, into liquid hydrocarbons may be accomplished by bringing it into contact with catalysts consisting of, or coated with, chromium or graphite at 800° to 1200° C. The catalysts are heated either indirectly or by an electric current passed through them.[89]

Benzene and other aromatic hydrocarbons are obtained from ethane, propane, or butane, or mixtures of these hydrocarbons, by passing them downwards through a brick-packed tower at 800° to 950° C. The velocity of the gases through the tower is adjusted according to the temperature in the various sections.[90]

Several processes of the Ruhrchemie A.-G. relate to the conversion of aliphatic hydrocarbons, such as methane, into aromatic hydrocarbons in two stages. In the first stage acetylene is formed and in the second stage this hydrocarbon is polymerized to aromatics. In one procedure,[91] a partial transformation of the aliphatic hydrocarbons to acetylene is effected by heating to temperatures exceeding 1600° C. for a very short heating period (less than 0.001 second). The resulting gas mixture is then heated for a longer period at 450° to 1000° C. In this second stage catalysts may be employed. The gases are heated electrically, and the heat of the exit gas is used to preheat the incoming gases or to generate steam. In the second stage the temperature is maintained by the heat content of the gas from the first stage. In a modification,[92] the gas is heated in the first stage to temperatures above 1120° C., at reduced pressure, for somewhat longer periods (not more than 0.5 second). The resulting gas mixture is then subjected to a second thermal treatment by passage through an apparatus having hot walls (e.g., at 580° C.) opposite cold walls (75° C.), which may be water-filled tubes. Catalysts, such as a mixture of aluminum oxide and potassium oxide, can be used.[93]

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[84] Wheeler, McAulay and Francis, British Patents 342,319, 1929, and 342,359, 1930; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 4889, 4890.

[85] British Patent 344,443, 1929; assigned to N. V. Silica en Oven-Mij.; *Chem. Abs.*, 1932, **26**, 150; French Patent 685,436, 1929; *Chem. Abs.*, 1930, **24**, 5764.

[86] British Patent 349,958, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1931, 788.

[87] British Patent 351,994, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1931, 960.

[88] British Patent 364,043, 1931; assigned to British and Dominions Feralloy Ltd.; *Brit. Chem. Abs.* **B**, 1932, 249. French Patent 719,190, 1931; *Chem. Abs.*, 1932, **26**, 3368.

[89] I. G. Farbenindustrie A.-G., British Patent 364,144, 1931; *Chem. Abs.*, 1933, **27**, 1637.

[90] Porter, U. S. Patent 1,777,894, Oct. 7, 1930; *Brit. Chem. Abs.* **B**, 1931, 667; U. S. Patent 1,895,086, Jan. 24, 1933; *Chem. Abs.*, 1933, **27**, 2459; both patents assigned to Continental Oil Co.

Coxon[94] developed a method for the thermal treatment of gaseous paraffin or olefin hydrocarbons in which the gases to be pyrolyzed are preheated by mixing with another heated gas. The mixed gases are then passed into the reaction zone where they are kept, for a short time, at the temperature necessary for the conversion reactions.

Wheeler[95] suggested that the hydrogen, formed simultaneously with aromatic hydrocarbons during the pyrolysis of methane or ethane, be removed from the gaseous products of pyrolysis before these are subjected to further thermal treatment. This may be accomplished in several ways, as for example, by leading the gases over copper oxide heated to 250° C., by diffusion, or by converting the hydrogen into methane by catalytic reaction with the requisite quantity of carbon monoxide.

The conversion of olefins into aromatic hydrocarbons for use in antiknock motor fuel is of importance in the possible utilization of vapor phase cracking gas which contains large proportions of lower olefins.[96] Conversion is effected in two stages. In the first stage the olefins are led over a hot catalyst (such as charcoal at 400° C.) at high pressures (e.g., 40 atmospheres). The liquid hydrocarbons are dehydrogenated in a second stage by passage over a catalyst of ammonium molybdate at 600° C. under 5 atmospheres pressure.

Other catalysts suggested for converting olefins into liquid hydrocarbons of low boiling point are, (1) gold, silver or copper in the form of turnings or gauze or as the lining of the reaction tube; (2) compounds of the alkali metals, particularly oxygen-containing compounds, to which may be added other metallic salts or oxides; and (3) salts of the acids of phosphorus, boron or antimony, their reduction products, or the acids or anhydrides themselves in the solid form supported on a carrier. Materials such as iron or nickel which promote the formation of carbon are excluded, as are also rough surfaces. For this reason the interior of the reaction vessel may be lined with copper, silver quartz or ferrosilicon or may be constructed of materials comprising free silica.[90a]

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[91] British Patent 373,249, 1931; *Brit. Chem. Abs.* **B**, 1932, 832. French Patent 711,515, 1931; *Chem. Abs.*, 1932, 26, 1938.

[92] British Patent 373,822, 1931; *Brit. Chem. Abs.* **B**, 1932, 832.

[93] British Patent 374,422, 1931; *Chem. Abs.*, 1933, 27, 3942; British Patent 374,055, 1931; *Brit. Chem. Abs.* **B**, 1932, 832.

[94] British Patent 347,017, 1931; assigned to Anglo-Persian Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 830.

[95] British Patent 324,939, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 406.

[96] I. G. Farbenindustrie A.-G., British Patent 261,393, 1926; *Brit. Chem. Abs.* **B**, 1928, 440.

[96a] I. G. Farbenindustrie A.-G., British Patent 376,397, 1932; *Chem. Abs.*, 1933, 27, 4066.

The gases should be free from sulphur. Methane, or gases containing or yielding methane, may be added and the residual gases after pyrolysis may be recirculated. At temperatures of 300° to 400° C. the products consist principally of liquid olefins and at 500° C. benzene and naphthenes predominate. The latter are converted to aromatics by catalytic dehydrogenation at temperatures above 500° C.[97] If desired, the olefins may be isolated first from the olefin-containing gas (by fractional liquefaction or absorption) and then converted into liquid hydrocarbons.[98]

Certain alloys have been proposed also as catalysts, among which may be mentioned brass, bronze, manganese-copper, or tinned, galvanized or chromium-plated iron and copper.[99]

Ramage[100] suggested passing water gas mixed with gaseous olefins, of not more than five carbon atoms per molecule, at atmospheric pressure through a series of tubes containing finely divided iron maintained at 537° to 965° C. (1000° to 1500° F.). The issuing gases contain large proportions of aromatic hydrocarbons which can be condensed or scrubbed out.

The conversion of mixtures of olefins and acetylene into higher hydrocarbons can be effected at high temperatures under any pressure without carbon deposition if the heated gases come into contact only with elements of Group IV (tin, silicon, lead, or carbon as graphite), or with zinc or aluminum or alloys of the latter metals. Thus, an oil is obtained when a mixture of ethylene and acetylene is led through an aluminum tube containing silicon and heated externally to a temperature of 525° to 600° C. At lower temperatures using a manganese-copper tube lined with tin, this gaseous mixture yielded a condensate containing about 13 per cent butadiene. Benzene hydrocarbons are obtained when tubes of manganese-copper or brass, lined with zinc, are employed.[101]

According to Wheeler and McAulay,[102] olefinic gases are converted into aromatic hydrocarbons by passage through tubes heated to temperatures above 1000° C. at space velocities exceeding 50 reciprocal minutes. For example, ethylene conducted at a space velocity of 6400 reciprocal minutes through a reaction zone maintained at 1100° C. gave about 30 per cent of light (aromatic) oil. The exit gases contained about 8 per cent acetylene.

For the production of higher-boiling olefinic or aromatic hydrocarbons,[103] gaseous olefins are heated under pressures as high as 1000 atmospheres at 350° to 800° C. in the presence of small pieces or bricks of elemental silicon or a ferro-silicon alloy containing a large proportion of silicon. The apparatus is made of materials resistant to the action of hydrogen sulphide and which do not catalyze the deposition of carbon. Such materials are "V2A" steel or steel containing molybdenum and tungsten or alloys of chromium and nickel. The operating conditions may be varied to produce a preponderance of either higher olefins or aromatic hydrocarbons. Egloff[103a] heats the gas which separates from the distillate resulting from the cracking of oils to about 650° to 1000° C. under superatmospheric pressure. The pressure is then lowered and the gases submitted to the action of ultraviolet light.

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[97] Wietzel and Pfaundler, U. S. Patent 1,910,910, May 23, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3942.

[98] I. G. Farbenindustrie A.-G., British Patent 291,137, 1927; *Brit. Chem. Abs.* **B**, 1928, 560. See also Mittasch, Pier, Wietzel and Langheinrich, U. S. Patents 1,913,940 and 1,913,941, June 13, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4390.

[99] I. G. Farbenindustrie A.-G., British Patent 309,199, 1927; *Brit. Chem. Abs.* **B**, 1929, 424. Winkler and Haeuber, U. S. Patent 1,894,255, Jan. 10, 1933; *Chem. Abs.*, 1933, **27**, 2454; Mittasch, Wietzel and Pfaundler, U. S. Patent 1,893,804, Jan. 10, 1933; *Chem. Abs.*, 1933, **27**, 2293; both patents assigned to I. G. Farbenindustrie A.-G. *Cf.* British Patent 269,593, 1926; *Brit. Chem. Abs.* **B**, 1928, 702.

[100] U. S. Patent 1,812,372, June 30, 1931; assigned to Coals and Chemicals, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 669; British Patent 335.353, 1929; *Chem. Abs.*, 1931, **25**, 1259; Canadian Patent 299,494, 1930; *Chem. Abs.*, 1930, **24**, 2866.

[101] I. G. Farbenindustrie A.-G., British Patent 316,422, 1928; *Chem. Abs.*, 1930, **24**, 1649.

[102] British Patent 332,998, 1929; assigned to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1931, **25**, 521.

[103] I. G. Farbenindustrie A.-G., 336,234, 1929; *Brit. Chem. Abs.* **B**, 1931, 10. Winkler and Haeuber, U. S. Patent 1,868,127, July 19, 1932; assigned to I. G. Farbenindustrie, A.-G.; *Chem. Abs.*, 1932, **26**, 5101.

Ethylene or its homologues are also polymerized by heating in the presence of an inert liquid such as mineral oils, vegetable oils, phenols, water or "Edeleanu extract".[103b] A high temperature and pressure are maintained. For example, ethylene is heated with paraffin oil to 420° C. under a pressure of 45 atmospheres.

Propylene, or gases containing 20 per cent or more of propylene, may be converted to aromatic hydrocarbons or acetylene by pyrolysis at 700° to 900° C. in an apparatus constructed of nickel-chromium steel or of silica.[104] Hercourt[104a] suggested a method for the removal of organic or mineral impurities from crude benzene and other hydrocarbons by bringing the liquids into contact with aluminum in the presence of steam. The aluminum is previously activated by traces of mercury or salts of mercury.

Rembert[104b] mixed crude oil in finely divided form with non-oxidizing gases preheated to above 1350° C., attaining almost instantaneously an equilibrium temperature above 500° C. The mixture was then passed through an elongated reaction zone, at the end of which the gases were led into a liquid such as oil or water to cool them instantly to stop reaction.

MANUFACTURE OF DIPHENYL

The pyrolysis of aliphatic hydrocarbons eliminates hydrogen from the molecule and forms various types of unsaturated hydrocarbons, followed (on continued pyrolysis) by cyclicization of the unsaturated hydrocarbons to yield aromatics and finally condensed or polycyclic compounds. In the preceding discussion, the reactions leading to the formation of aromatic hydrocarbons have been considered in some detail. Such reactions include not only dehydrogenation and cyclicization but also in many instances a splitting of the molecule with the simultaneous formation of hydrocarbons of low molecular weight (e.g., methane, ethane and ethylene). Aromatic hydrocarbons, unless they have aliphatic side-chains, do not exhibit such reactions, but undergo condensation accompanied by the elimination of hydrogen.

In 1866 Berthelot[105] observed that benzene vapors when passed through a red-hot tube are converted to a considerable extent into diphenyl, according to the reaction:[106]

$$2C_6H_6 \longrightarrow C_6H_5C_6H_5 + H_2$$

The production of this hydrocarbon, however, has been put on a commercial basis only during the past decade. In the petroleum industry diphenyl has been employed as a material for high temperature vapor phase heat transfer.[107] A eutectic mixture of 26 per cent diphenyl and 74 per cent of diphenyl oxide[108] as well as mixtures of diphenyl and naphthalene[109] have been suggested for the same purpose.

[103a] U. S. Patent 1,904,362, April 18, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 3601.

[103b] Bataafsche Petroleum Maatschappij, British Patent 331,186, 1929; *Chem. Abs.*, 1931, **25**, 114; French Patent 690,935, 1930; *Chem. Abs.*, 1931, **25**, 1259.

[104] Groll, British Patent 369,351, 1930; assigned to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1932, 670. French Patent 725,114, 1931; *Chem. Abs.*, 1932, **26**, 4823.

[104a] French Patent 736,378, 1931; *Chem. Abs.*, 1933, **27**, 1499.

[104b] U. S. Patent 1,892,534, Dec. 27, 1932; assigned to Tidewater Oil Co.; *Chem. Abs.*, 1933, **27**, 2293.

[105] *Ann. chim.*, 1866, (4) **9**, 454; *Bull. soc. chim.*, 1866, (2) **6**, 274; *Compt. rend.*, 1866, **63**, 789; *Ann.*, 1867, **142**, 252.

[106] This reaction was investigated also by Schmidt and Schultz. *Ber.*, 1872, **5**, 682; *Ann.*, 1880, **203**, 118; Olgiati, *Ber.*, 1894, **27**, 3387; McKee, *J.S.C.I.*, 1904, **23**, 403; Smith and Lewcock, *J.C.S.*, 1912, **101**, 1453; Rittman, Byron and Egloff, *Ind. Eng. Chem.*, 1915, **7**, 1019; Zanetti and Egloff, *Ind. Eng. Chem.*, 1917, **9**, 350. The equilibrium constants of this reaction at temperatures of 845°, 900°, and 920° C. have been determined by Vvedenskii and Frost, *J. Gen. Chem.* (*Russia*), 1932, **2**, 542; *Chem. Abs.*, 1933, **27**, 888.

The manufacture of diphenyl has been described by Scott.[110] Benzene vapor is passed through a metal coil immersed in a lead bath maintained at 600° to 650° C. As the vapors leave the coil they bubble up through the molten lead into a similar coil which is immersed in a second lead bath kept at 750° to 800° C. The diphenyl so produced is conducted at a high velocity into a water-cooled condenser. In another process the benzene vapors are led through a reaction chamber at 800° C. containing contact agents which minimize the deposition of carbon.[111] Such substances are the sulphides of cobalt, iron, copper, molybdenum, arsenic, tin or zinc; the chlorides of nickel or antimony, potassium chromium sulphate, or the metals selenium, arsenic, silicon, antimony, or molybdenum. Other catalysts which have been suggested for the dehydrogenation include difficultly fusible oxides, vanadates, chromates, tungstates, molybdates, aluminates, and zincates, such as those of calcium, magnesium, titanium, cerium, zirconium, thorium and beryllium.[111a]

Govers[112] used a bath of molten cryolite or other non-metallic liquid at 750° C., and heated the benzene vapor to 650° C. prior to its passage through these liquids. A conversion of eight per cent was obtained. In another process[113] the vapors of benzene are brought into contact with a catalyst, consisting of 80 parts of potassium carbonate, 50 parts of thorium oxide and 5 parts of cobalt oxide, maintained at a temperature of 760° C.

An apparatus for this reaction has been described also by Hixon and his collaborators.[114] Their results indicated that the optimum temperature for the conversion is about 740° C. The yields of diphenyl in all instances were increased by using pressures greater than atmospheric. At a temperature of 740° C., a pressure of 8 atmospheres, and a rate of flow of about 400 cc. of benzene vapor per 164 cc. of available reaction space per hour, about 20 per cent of the benzene is pyrolyzed to diphenyl. Under the same conditions the chemical efficiency of the process may reach 98 per cent, i.e., only a negligible formation of by-products occurs. Increasing the rate of flow decreases the proportion of diphenyl formed. Complex diaryl compounds having boiling points higher than diphenyl are obtained by vaporizing pure commercial benzene or commercial 90 per cent benzene.[114a] The benzene is first heated to a temperature just below that at which diaryl compounds are formed, and is then rapidly raised to a point at which complex diaryl compounds result.

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[107] As a heat transfer substance in the manufacture of lubricants, see Reid, *Refiner*, 1929, **8** (10), 63; 1930, **9** (1), 98. For the same purpose in other industries, see Badger, Monrad and Diamond, *Ind. Eng. Chem.*, 1930, **22**, 700; Montillon, Rohrbach and Badger, *ibid.*, 1931, **23**, 763. For the thermal properties of diphenyl, see Chipman and Peltier, *Ind. Eng. Chem.*, 1929, **21**, 1106.

[108] Grebe, *Chem. Met. Eng.*, 1932, **39**, 213.

[109] Dow, U. S. Patent 1,893,051, Jan. 3, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 2227.

[110] British Patent 312,902, 1929; assigned to Federal Phosphorus Co.; *Brit. Chem. Abs.* **B**, 1930, 453; U. S. Patent 1,894,283, Jan. 17, 1933; assigned to Swann Research Inc.; *Chem. Abs.*, 1933, **27**, 2459. Also, Durgin and Jenkins, U. S. Patent 1,894,266, Jan. 17, 1933; assigned to Swann Research Inc.; *Chem. Abs.*, 1933, **27**, 2459. The formation of analogous compounds from toluene and from xylene in a similar manner has been described by Carothers and Scott, British Patent 338,631, 1929; assigned to Federal Phosphorus Co.; French Patent 37,449, 1929, addition to French Patent 667,840; *Chem. Abs.*, 1931, **25**, 2436.

[111] Federal Phosphorus Co., French Patent 715,017, 1931; *Chem. Abs.*, 1932, **26**, 1626.

[111a] I. G. Farbenindustrie A.-G., British Patent 356,189, 1930; *Brit. Chem. Abs.* **B**, 1932, 95.

[112] British Patent 341,024, 1929; *Brit. Chem. Abs.* **B**, 1931, 386. French Patent 683,230, 1929; *Chem. Abs.*, 1930, **24**, 4524.

[113] I. G. Farbenindustrie A.-G., British Patent 369,613, 1930; *Chem. Zentr.*, 1932, **2**, 925.

[114] Hixon, Work, Alessandroni, Clifford and Wilkens, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 289.

[114a] Federal Phosphorus Co., German Patent 581,046, 1933; *Chem. Abs.*, 1933, **27**, 5082; French Patent 37,449, 1929; *Chem. Abs.*, 1931, **25**, 2436; addition to French Patent 667,840, 1929; *Chem. Abs.*, 1930, **24**, 1394.

Chapter 6

Action of Aluminum Chloride on Hydrocarbons

Many examples of the pronounced influence exerted by various catalysts on the thermal reactions of hydrocarbons have been noted in the preceding pages. Anhydrous aluminum chloride, however, is unique in this respect and therefore it is desirable to discuss its effect on the thermal decomposition of each series of hydrocarbons separately. Aluminum chloride induces molecular disintegration of higher hydrocarbons at relatively low temperatures, the products being low-boiling saturated hydrocarbon oils. It is also an active agent for polymerizing unsaturated hydrocarbons, though at higher temperatures the decomposition reaction (producing low-boiling paraffin hydrocarbons) occurs simultaneously with that of polymerization. Whatever may be the mechanism of catalysis by other active bodies, the action of aluminum chloride is a purely chemical process through reactions forming double compounds with certain hydrocarbons, probably unsaturated ones.

Friedel and Crafts, whose names are associated with certain classic reactions catalyzed by aluminum chloride, were the first to notice that it might be employed in the production of light oils from heavier ones by cracking.[1] In 1881 Gustavson [2] found on treating hydrocarbons obtained by fractionating American gasoline or Caucasian kerosene with anhydrous aluminum bromide and hydrobromic acid that two layers were formed. The lower layer had the approximate composition $AlBr_3 \cdot C_4H_8$ and decomposed at 120° C. to yield gaseous hydrocarbons.

Since that time, processes for the production of gasoline from heavy petroleum fractions using aluminum chloride have been developed by the Continental Caoutchouc and Gutta Percha Co.,[3] Gray,[4] Cobb,[5] Koetschau,[6] Heusler,[7] Alexander and Taber [8] and by McAfee, whose processes, mentioned below, have been used in a commercial way.

PRODUCTION OF GASOLINE WITH ALUMINUM CHLORIDE

The two most important processes advocated for the production of gasoline from heavier oils by treatment with aluminum chloride are those of Gray and of McAfee. The latter process has been exploited by the Gulf Refining Co. and the former by The Texas Company. Gray stated in the description of his process that the low-boiling products of the reaction possess end-points approximately the same as the temperature at which the decomposition is effected, and in operating at a temperature of 550° to 600° F. (288° to 316° C.) a dephlegmator should be used to return the higher-boiling fractions to the still.

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[1] British Patent 4,769, 1877, to Abel; *Chemische Industrie*, 1878, 1, 411. See Heusler, *Z. angew. Chem.*, 1896, 9, 288. *Cf.* Friedel and Gorgeux, *Compt. rend.*, 1898, 127, 590; *Chem. Soc. Abs.*, 1899, 76 (1), 181.

[2] *Ber.*, 1881, 14, 2619; *Chem. Soc. Abs.*, 1882, 42, 374. *J. Russ. Phys.-Chem. Soc.*, 1880, 13, 149; *Chem. Zentr.*, 1881, 353; *Chem. Soc. Abs.*, 1882, 42, 27.

[3] British Patent 7,112, 1914; *J.S.C.I.*, 1915, 34, 826. French Patent 469,948, 1914; *J.S.C.I.*, 1915, 34, 19.

[4] U. S. Patents 1,193,540 and 1,193,541, Aug. 8, 1916; *Chem. Abs.*, 1916, 10, 2402. British Patents 17,838 and 17,839, 1913; *J.S.C.I.*, 1914, 33, 1044. Canadian Patents 152,216 and 152,217, 1913; *Chem. Abs.*, 1914, 8, 1344.

[5] U. S. Patents 1,322,762 and 1,322,878, Nov. 25, 1919; assigned to Standard Oil Co. of New Jersey; *J.S.C.I.*, 1920, 39, 98A.

[6] U. S. Patent 1,325,299, Dec. 16, 1919; *Chem. Abs.*, 1920, 14, 466.

[7] German Patent 83,494; 1894; *Chem. Zentr.*, 1895, 2, 1142.

[8] U. S. Patent 1,381,098, June 14, 1921; assigned to Gulf Refining Co.; *J.S.C.I.*, 1921, 40, 839A.

McAfee emphasized not only the conversion of high-boiling hydrocarbons to lower-boiling ones but also the improvement in the quality of the residue in the reaction vessel. For a description of the McAfee process and an account of its numerous details the original references should be consulted.[9] The operation is conducted by adding 5 to 8 per cent of anhydrous aluminum chloride to the oil, previously dried at 300° to 350° F. (150° to 175° C.) for some time, and heating the mixture to 550° F. (290° C.) or higher in a still fitted with a stirring device. A differential condenser returns all the products of the reaction except those of desired volatility. It is possible to obtain from 15 per cent to as high as 60 per cent yields of gasoline, consisting principally of saturated hydrocarbons, from a single distillation whose period is limited by various factors to 24 to 48 hours. Because aluminum chloride sublimes at 181°-185° C., sustained high temperatures cause a loss of catalyst, which can be avoided by pressure operation.

Some details of the reactions taking place during such a process have been supplied by Dubrov, Lavrovsky, Goldstein, Fish and Mikhnovskaya.[10] In addition to the splitting of the larger molecules into smaller ones, polymerization, rearrangement and carbonization take place simultaneously; and because of the content of hydrogen in the original hydrocarbons, the maximum yield of light products which can be expected is limited to 70 per cent. The gasolines so produced contain large percentages of saturated hydrocarbons of the naphthene and aromatic types; in one instance analysis indicated that the gasoline contained about 5 per cent aromatics, 41 per cent naphthenes, and 38 per cent paraffins. The residual oils after the distillation of the gasoline and kerosene fractions are said to be high grade lubricants of a saturated character.

The rate of decomposition of the oil by aluminum chloride is materially decreased by the presence of potassium and, particularly, sodium compounds. On the other hand, as much as 1 per cent of ferric chloride, silicon tetrachloride or aluminum oxide does not affect the yield. About 10 per cent of aluminum chloride is used in the preparation of gasoline, but about 5 per cent is sufficient when lubricating oils of high viscosity-index and low pour points are desired. It was noted also that paraffin wax which had been treated with aluminum chloride readily yielded solid acids on oxidation. Waterman and van Soest[11] obtained small yields of gasoline (18 to 23 per cent) on cracking Rangoon paraffin wax with aluminum chloride.

After treatment with aluminum chloride and removal of the products, the residue in the still consists of granular coke of little value containing aluminum chloride,[12] and heavy oils which can be worked up into lubricating and similar oils.

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[9] *Ind. Eng. Chem.*, 1915, **7**, 737; *Refiner*, 1928, **8** (8), 57. Also the following U. S. Patents assigned to the Gulf Refining Co.: 1,099,096, June 2, 1914; 1,127,465, Feb. 9, 1915; 1,144,304, June 22, 1915; 1,202,081, Oct. 24, 1916; 1,206,874, Dec. 5, 1916; 1,217,471, Feb. 27, 1917; 1,235,523, July 31, 1917; 1,277,092, 1,277,328 and 1,277,329, Aug. 27, 1918; 1,326,072 and 1,326,073, Dec. 23, 1919; 1,405,054, Jan. 31, 1922; 1,405,734, Feb. 7, 1922; 1,424,574, Aug. 1, 1922; 1,476,091, Dec. 4, 1923; 1,478,444, Dec. 25, 1923; 1,482,438, Feb. 5, 1924; 1,501,014, July 8, 1924; 1,534,130, Apr. 21, 1925; 1,543,934 and 1,544,328, June 30, 1925; 1,568,171, Jan. 5, 1926; 1,578,052 and 1,578,053, Mar. 23, 1926; 1,608,328 and 1,608,329, Nov. 23, 1926; 1,636,144, July 19, 1927; McAfee and Roberts, 1,690,990, Nov. 6, 1928; 1,814,397, July 14, 1931. McAfee and Barnes, 1,774,559, Sept. 2, 1930. *Cf.* also Prichard and Henderson, 1,476,219, Dec. 4, 1923, and 1,577,871, Mar. 23, 1926; both assigned to Gulf Refining Co. See also Stevens and Adams, U. S. Patent 1,915,206, June 20, 1933; assigned to Gulf Refining Co.; *Chem. Abs.*, 1933, **27**, 4385.

[10] *Neft. Khoz.*, 1932, **22**, 19; *Chem. Abs.*, 1932, **26**, 2853, 4941.

[11] *J. Inst. Pet. Tech.*, 1928, **14**, 756; *Chem. Abs.*, 1929, **23**, 967.

Graetz[13] treated dehydrated and refined Gabian petroleum (initial boiling point 217° C.) with increasing amounts of aluminum chloride; he obtained a maximum yield (about 75 per cent) of products distilling up to 210° C. with 9 per cent of aluminum chloride. With crude petroleum, the same maximum amount of light products was found but 14 to 15 per cent of aluminum chloride had to be used. This was due to the effect of water, sulphur and oxygenated compounds in the crude. He maintains that the mechanism of the cracking is first, the formation of a hydrocarbon-metal chloride complex and second, breaking of the complex at the distillation or decomposition temperature of the metal chloride accompanied by the severing of the carbon chain. The minimum cracking temperature of oil is 160° C.; at 200° C. the reaction is fairly fast. The aluminum chloride complex is stable up to 180°-190° C., it is fairly active at 190°-210° C. and completely decomposed at 230°-240° C. It would therefore be better, according to Graetz, to carry out the cracking at 240° to 245° C. He also found that sulphur, stannic, mercuric, cupric, ferric and sodium chlorides form complexes with oil on heating for some time, but in order that cracking may be catalyzed by a metal chloride the latter must be volatilizable or decomposable between 190° and 210° C. The complexes formed by chlorides boiling at a lower temperature (sulphur chloride and stannic chloride) decompose below the minimum cracking temperature; the high-boiling chlorides such as ferric chloride are very stable so that cracking cannot take place below 250°-260° C.

The economic success of any of these processes depends largely upon the cost of the aluminum chloride.[14] Methods have been developed for producing this material at a cost low enough to permit of its extensive use in the industries.[15] Aluminum chloride was first prepared by Oerstedt[16] by passing dry chlorine gas over alumina mixed with powdered charcoal and ignited in a porcelain tube. It was from this compound that Wöhler[17] succeeded in isolating the element. He also observed that on heating aluminum to redness in a current of chlorine, aluminum chloride was formed and sublimed, a method still used for the preparation of the purest samples.

A general procedure for obtaining anhydrous chlorides by heating the oxide of the metal with phosgene was proposed by Chauvenet.[18] The treatment of oxide ores with carbon monoxide or carbon, and chlorine or with phosgene was described by Brode and Wursten,[19] Alexander,[20] McAfee,[21] and McAfee and Roberts.[22]

McAfee[23] described the large-scale production of this material by the Gulf

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[12] Sludge obtained from previous operations may be used instead of fresh aluminum chloride according to Tilicheyev and Kuruindin; *Neft. Khoz.*, 1930, 1, 586; *Brit. Chem. Abs.* **B**, 1931, 1081.

[13] *Ann. office nat. comb. liquides*, 1927, **2**, 69; *Chem. Abs.*, 1927, **21**, 3737.

[14] See Simon, *Chimie et Industrie*, 1930, **24**, 1317; *Brit. Chem. Abs.* **B**, 1931, 245.

[15] For a historical account of methods of preparing aluminum chloride see Kränzlein, "Aluminumchlorid in der organischen Chemie," Verlag Chemie, G.m.b.H., Berlin, **1932**, 9.

[16] *Poggendorff's Ann.*, 1825, **5**, 132; *cf.* Ferussac, *Bull. Sci. Mathem.*, 1826, 275.

[17] *Poggendorff's Ann.*, 1827, **11**, 146.

[18] *Compt. rend.*, 1911, **152**, 87; *Chem. Soc. Abs.*, 1911, **100** (2), 109.

[19] I. G. Farbenindustrie A.-G., German Patent 502,844. 1925; *Chem. Abs.*, 1930. **24**. 5441. See German Patents 525,186 and 525,560, 1927; additions to 502.884; *Chem. Abs.*, 1931. **25**. 4365. 4668; also see German Patent 524,712, 1926; U. S. Patent 1,809,158, June 9, 1931; *Chem. Abs.*, 1931, **25**, 4365.

[20] U. S. Patent 1,366,626. Jan. 25. 1921; *J.S.C.I.*, 1921, **40**, 179A.

[21] U. S. Patents (all assigned to Gulf Refining Co.) 1,217,471, Feb. 27, 1917; *J.S.C.I.*, 1917, **36**, 456; 1,543.934 and 1,544,328, June 30, 1925; *J.S.C.I.*, 1925, **44**, 671B; 1,578,052, March 23, 1926; *Brit. Chem. Abs.* **B**, 1926. 439.

[22] U. S. Patent 1,690,990. Nov. 6. 1928; assigned to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1929. 54; see also McAfee. U. S. Patent 1,814,397, July 14, 1931; assigned to Gulf Refining Co.; *Chem. Abs.*, 1931. **25**. 5255.

[23] *Refiner*, 1928, **8** (8), 57; *Ind. Eng. Chem.*, 1929, **21**, 670.

Refining Co. Crude bauxite ore is calcined in an internally heated rotary kiln at about 1800° F. (980° C.) to drive off moisture. It is then mixed with coking coal in the proportion of 1 part of coal to 3 parts of bauxite by weight; the mixture is pulverized, mixed with a liquid binder and briquetted; and the briquettes are preheated to about 1500° F. (815° C.) to expel volatile matter, forming a hard composition of 82 per cent bauxite and 18 per cent carbon. The hot briquettes are charged into a vertical chlorinating furnace, and the temperature is raised to 1600° F. (870° C.) by a short air-blow, after which chlorine is passed downwards through the charge for 8 to 10 hours. Aluminum chloride passes from the bottom to a firebrick cooler and is deposited as a powder, 75 per cent passing a 10-mesh screen.[4]

The disadvantages of treatment with aluminum chloride as a refining process are the cost of the reagent, the production of corrosive hydrogen chloride fumes during the process, and the difficulties of disposing of the coke residues. The gasolines produced by this process, however, contain mainly saturated hydrocarbons and are therefore more stable toward oxidation than those from the usual cracking operation. The use of other anhydrous chlorides such as ferric chloride, antimony chloride, stannic chloride, titanium chloride, and zinc chloride has been investigated[24] but none of these is known to be used at present.

Lidov[25] found that in the production of low boiling hydrocarbons from high boiling ones it is advantageous to form the anhydrous catalyst during the process. For example, solar oil is mixed with iron or with aluminum, heated for 2 to 3 hours at 250° to 280° C., and during this time a current of dry hydrogen chloride gas is passed into the mixture. In this manner a yield of 65 per cent of benzine, of specific gravity 0.865, is obtained with iron and 75 per cent with aluminum. The highest yield of aromatic compounds is obtained by operating at 600° C. and under a pressure of 18 atmospheres. Bespolov and Degtyareva[25a] investigated the possibilities of refining cracked gasoline with aluminum chloride. They found at least 1 per cent by weight of aluminum chloride necessary to produce a marketable gasoline. The sulphur content was reduced by about 50 per cent, but gum formation and odor increased in storage.

ACTION OF ANHYDROUS ALUMINUM CHLORIDE ON PARAFFIN HYDROCARBONS

Pictet and Lerczynska[26] treated various higher fractions of American and Russian petroleum with 10 per cent of aluminum chloride and obtained benzine fractions corresponding to almost pure paraffin hydrocarbons. When the residuum had been freed from aluminum chloride by washing with water, there remained a black pitch, resembling asphalt, partly soluble in alcohol and ether and completely soluble in chloroform. Analysis of this pitch showed it to consist of 92.2 per cent carbon and 7.2 to 7.6 per cent hydrogen, corresponding to the empirical formula C_nH_n. Pictet and Lerczynska were of the opinion that aluminum chloride caused the splitting off of side chains from naphthene hydrocarbons and polymerization of the unsaturated residue. Zelinsky[27] obtained similar results with heavy petroleum oils and also found that the lower fraction (boiling up to 70° C.) of the gasoline obtained by the aluminum chloride process consisted largely of paraffin hydrocarbons. The lower petroleum fractions boiling up to 125° C. were found to be much more resistant to the action of the chloride than the higher ones. Naphthenes were entirely absent from the products of the action of aluminum chloride on paraffin wax, only paraffin hydrocarbons being present.

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[24] See, for example, Stanley, *J.S.C.I.*, 1930, **49**, 349T. Pictet and Lerczynska, *Bull. soc. chim.*, 1916, **19**, 326. Menschutkin, *J. chim. phys.*, 1911, **9**, 538; *Chem. Soc. Abs.*, 1911, **100** (1), 992.

[25] *Petroleum*, 1917, **12**, 413; *Chem. Abs.*, 1919, **13**, 3005.

[25a] *Azerb. Neft. Khoz.*, 1931, Nos. 11-12, 88-90; *Chem. Abs.*, 1932, **26**, 2309.

[26] *Bull. soc. chim.*, 1916, **19**, 326; *Chem. Soc. Abs.*, 1916, **110** (1), 785.

[27] *Techn. Wirtschaftl. Nachr.*, 1922, 193; *Chem. Zentr.*, 1923, **1**, 476; *Chem. Abs.*, 1924, **18**, 1746.

Comprehensive study of the behavior of aluminum chloride with hydrocarbons was conducted by Grignard and Stratford[28] who determined the action of 20 to 30 per cent of this reagent on various pure hydrocarbons at temperatures ranging from 120° to 150° C. All the paraffin hydrocarbons studied, namely octane, diisobutyl, decane, diisoamyl, and heptadecane, split off n-butane. When the molecule contained ten or more carbon atoms butane was split off simultaneously from both ends. The unsaturated residues polymerized with the production of complex hydrocarbons.

Cox[29] found that when nonane was heated for 8 hours at 110° to 120° C. with aluminum chloride, butane was produced, and concluded that the residual pentene was partly converted into cyclopentane, this view being supported by the fact that cyclopentane is not affected by heating with aluminum chloride.

Further work on the action of aluminum chloride on the paraffin hydrocarbons was reported by Jurkiewicz and Kling.[30] Decomposition was effected in sealed glass tubes over the temperature range 250° to 500° C. Methane was not converted into higher hydrocarbons but hydrogen was evolved and carbon deposition was noticed at 500° C. Ethane began to decompose at 320° C. and at 410° C. the formation of oily substances and carbon had begun, becoming appreciable at 500° C. These oily substances, which were considered to be addition compounds of aluminum chloride and hydrocarbons, were encountered also with other hydrocarbons studied. Synthesis of higher hydrocarbons from isobutane was noted at 245° C. The temperature range 370° to 390° C. was considered to be a critical one, above which the reaction of aluminum chloride is no longer specific. The observation was made that the resistance of paraffin hydrocarbons to the action of aluminum chloride decreases with increasing molecular weight.

Schneider[31] studied the action of aluminum chloride on hexane and isohexane and found that a synthesis of more complex molecules occurs, as well as decomposition to smaller ones. The gaseous decomposition products consisted of butane, a little propane, pentane and unchanged hexane, but no methane. The liquid residues consisted of hydrocarbons boiling higher than the original material. Unsaturated hydrocarbons were retained in the aluminum chloride sludge and were recovered by decomposing it with ice water.

Butane was reported[32] as the principal constituent of the gas produced by the action of aluminum chloride on various Russian petroleum oils.

Summing up, therefore, we may conclude that the lower paraffin hydrocarbons are relatively resistant to the action of aluminum chloride, the synthesis to higher hydrocarbons taking place at elevated temperatures accompanied by some decomposition. The higher hydrocarbons, on the other hand, react at much lower temperatures and tend to split off lower hydrocarbons (chiefly butanes) followed by polymerization of the unsaturated residues.

ACTION OF ANHYDROUS ALUMINUM CHLORIDE ON OLEFINS

The chief action of aluminum chloride on olefins is one of polymerization but this reaction may be obscured by extensive decomposition resulting in the formation of lower paraffins and higher-boiling hydrocarbons of lower percentage hydrogen than the original hydrocarbon.[33] At ordinary temperature and pressure anhydrous aluminum chloride slowly adsorbs ethylene but most of the olefin is recovered on heating, only a small amount of residual red oil being obtained.[34] Isobutene and aluminum chloride yield colorless oils, and also dark red oils which contain 11.5 per cent aluminum and further react with isobutene. Leenderste, Tulleners and Waterman[35] observed that the chloride has very little effect on isopropylethylene at —80° C. A slight rise in the temperature, however, brought about the formation of viscous and sticky polymerized bodies.

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[28] *Compt. rend.*, 1924, 178, 2149; *Chem. Soc. Abs.*, 1924, 126 (1), 841.

[29] *Bull. soc. chim.*, 1925, 37, 1549; *Chem. Abs.*, 1926, 20, 899.

[30] *Przemysl Chem.*, 1929, 13, 481; *Chem. Abs.*, 1930, 24, 1338.

[31] *Abstracts Sci. Tech. Publications, Mass. Inst. Tech.*, 1928, 72. See also Thesis, Mass. Inst. Tech., 1931; *ibid.*, 1931, 55; *Chem. Abs.*, 1931, 25, 5175.

[32] Dubrov, Lavrovsky, Goldstein, Fish and Mikhnovskaya, *loc. cit.*

Szayna[36] investigated the reaction between the lower olefins and aluminum chloride. He noted that ethylene reacted with difficulty at 100° C. and 150° C., yielding only small quantities of condensed products. Under similar conditions other olefins gave a gas, liquid hydrocarbons, and an organo-metallic compound. The gas was composed exclusively of butane. The lower-boiling liquids were chiefly paraffins and the heavier fractions consisted of cycloparaffins together with small amounts of unsaturated hydrocarbons. The organo-metallic compound was a dark brown viscous oil, decomposable by water, and had the empirical formula $AlCl_3(C_4H_x)_n$. The oil from this complex, after hydrolysis, corresponded with either $(C_8H_{12})_n$ or $(C_8H_{18})_n$, and its properties indicated the presence of cyclic unsaturated hydrocarbons.

Ipatiev and Rutala[37] studied the influence of catalysts, such as aluminum and zinc chlorides, on the condensation of ethylene under pressure. In the presence of zinc chloride at 70 atmospheres pressure polymerization took place at 275° C., the liquid products consisting of pentane, isopentane, hexane and higher paraffins, together with olefins of 6 to 9 carbon atoms.[38] Under 70 atmospheres pressure at ordinary temperature freshly prepared aluminum chloride induced polymerization to a greenish-red liquid containing paraffins in the lower fractions. At 200° C., only a carbonaceous residue was obtained. Prior to the work of Ipatiev and Rutala on ethylene, the polymerizing effect of aluminum chloride on other unsaturated hydrocarbons had been demonstrated by Heusler,[39] and the polymerization of amylene in the presence of that reagent had been studied by Aschan[40] and by Engler and Rutala.[41] The latter investigators found that the lower-boiling products consisted chiefly of paraffins, the cycloparaffins predominating in the fractions boiling above 175° C. Furthermore, they obtained an oil containing 87 per cent carbon, having a composition corresponding to C_nH_{2n-6} and possessing the properties of naturally occurring lubricating oil.[42] Steinkopf and Freund[43] observed that the reaction of aluminum chloride on turpentine oil yields products of a nature similar to those obtained from straight-chain olefins.

Stanley[44] examined the reaction between aluminum chloride and ethylene under pressures up to 50 atmospheres at ordinary and elevated temperatures in the presence of a diluent such as aromatic-free petroleum ether. At ordinary temperatures the reaction was rather slow, and yielded a free oil (an oil not combined with aluminum chloride) and a viscous, pasty organo-metallic compound from which some oil which had combined was obtained on decomposition with water. The free oil consisted mostly of liquid saturated hydrocarbons containing from 10 to 45 carbon atoms per molecule. The lower-boiling fractions were paraffins but the main part of the oil consisted of saturated hydrocarbons of the formula C_nH_{2n}, presumably cycloparaffins. The oil liberated from the organo-metallic compound consisted of a complex mixture of hydrocarbons with from 10 to more than 50 carbon atoms per molecule, apparently unsaturated and containing less hydrogen than required by the formula C_nH_{2n}. The oil was regarded as being composed of unsaturated hydrocarbons of the olefin series mixed with hydrocarbons of lower hydrogen content (probably unsaturated cyclic hydrocarbons). Stanley found that the condensation of ethylene under pressure was much more rapid at higher temperatures but the life of the catalyst was shortened under these conditions and gaseous paraffin hydrocarbons appeared. As before, free oil and aluminum chloride double compounds were formed but these differed considerably from the products obtained at lower temperatures. The organo-metallic complex tended to contain greater proportions of combined carbon with rising temperature. The free oil formed at higher temperatures was clear and contained large proportions of low-boiling constituents. The low-boiling fractions consisted of paraffin hydrocarbons of five or more carbon atoms. The higher-boiling fractions contained compounds deficient in hydrogen corresponding to the formulas C_nH_{2n-6}, C_nH_{2n-8}, and C_nH_{2n-10}, probably polynuclear naphthenes. The primary reaction was considered to be polymerization to higher olefins which combined with the aluminum chloride to form organo-metallic complexes. Isomerization of some of the higher olefins to the corresponding cycloparaffins sufficed to explain the formation of the saturated free oil at lower temperature. At higher temperatures the processes of polymerization and isomerization were attended by extensive decomposition, resulting in the splitting off of lower paraffins with subsequent polymerization of the unsaturated residues. These three reactions, namely, polymerization to higher olefins, isomerization of these olefins to the corresponding cycloparaffins, and the splitting off of lower paraffin molecules from the more complex hydrocarbon molecules, are undoubtedly the principal changes which occur through the action of aluminum chloride on olefin hydrocarbons.

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[33] For a review of theories of polymerization see Carothers, *Chem. Reviews*, 1931, 8, 353.

[34] Hunter and Yohe, *J.A.C.S.*, 1933, 55, 1248.

[35] *Rec. trav. chim.*, 1933, 52, 515.

[36] *Przemysl Chem.*, 1928, 12, 637; *Chem. Abs.*, 1929, 23, 1384.

[37] *Ber.*, 1913, 46, 1748.

[38] Unsaturated hydrocarbons of high molecular weight are said to be produced by contacting olefins at high temperatures, but below 300° C., for about 100 seconds with aluminum chloride; I. G. Farbenindustrie A.-G., French Patent 718,346, 1931; *Chem. Abs.*, 1932, 26, 2986. Also Pure Oil Co., French Patent 680,038, 1929; *Chem. Abs.*, 1930, 24, 3799; recommends the use of temperatures of 260° to 540° C. with pressures of 40 to 120 atmospheres for polymerization of ethylene and propylene.

[39] *Z. angew. Chem.*, 1896, 9, 288, 218.

[40] *Ann.*, 1902, 324, 26.

[41] *Ber.*, 1909, 42, 4610, 4620.

[42] *Ber.*, 1910, 43, 388; also Engler and Halmai, *ibid.*, 1910, 43, 397.

[43] *Ber.*, 1914, 47, 411.

[44] *J.S.C.I.*, 1930, 49, 349T. See also Nash, *Chem. Age (London)*, 1932, 26, 234; and Nash, Stanley and Bowen, *Pet. Times*, 1930, 24, 799; *J. Inst. Pet. Tech.*, 1930, 16, 830; *Chem. Abs.*, 1931, 25, 1664.

Henderson and Gangloff[45] isolated numerous compounds of olefins and aluminum chloride formed by passing the unsaturated hydrocarbon into a solution of aluminum chloride in methyl or ethyl alcohol. Thus, in methyl alcohol ethylene formed a substance of the approximate formula $AlCl_3 \cdot C_2H_4 \cdot CH_3OH \cdot H_2O$, and amylene gave $AlCl_3 \cdot C_5H_{10} \cdot CH_3OH$. There appears to be little doubt, according to these investigators, that in the catalytic oil-cracking processes, the catalyst combines with certain products of the reaction, thus preventing the distillation of the unsaturated portion of the oil.

The polymerizing action of aluminum chloride on olefins requires special consideration on account not only of the theoretical interest associated with the reaction but also of the great technical importance which processes of this character are assuming, particularly in the production of synthetic lubricants. The action of aluminum chloride on hydrocarbons is undoubtedly a special case of the Friedel-Crafts reaction, which is also catalyzed by other anhydrous chlorides.

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[45] *J.A.C.S.*, 1916, **38**, 1382; 1917, **39**, 1420.

Thus, Pictet and Lerczynska[46] found that anhydrous ferrous or ferric chlorides could be similarly used in the cracking of hydrocarbons; but their action is weaker and requires higher temperatures than aluminum chloride.[47]

The polymerization of gaseous olefins by aluminum chloride to yield viscous oils capable of use as lubricants is receiving attention, especially in countries where supplies of crude petroleum are not available. The question of the production of synthetic lubricants is discussed in a separate section later.

Although this discussion has been restricted largely to the action of aluminum chloride on olefins, it should be noted that the polymerizing action of zinc chloride has been investigated by Kondakov[48] and that of boron trifluoride by Butlerov and Gorianov[49] and by Otto and his associates.[50] According to Otto,[51] oils which very closely resemble lubricating oils in their flash points and viscosities result from the polymerization of ethylene in the presence of boron fluoride. These polymerizations, however, are discussed with greater detail in Chapter 26.

ACTION OF ANHYDROUS ALUMINUM CHLORIDE ON CYCLOPARAFFINS

According to Gurwitsch and Moore,[52] naphthenes combine with aluminum chloride to form orange-colored viscous liquids, which are decomposed by water to yield condensation products, cyclopentane derivatives being decomposed more quickly than cyclohexane derivatives. On the other hand, Cox[53] found that cyclopentane is not affected by heating to 110° to 120° C. with aluminum chloride and Koetschau[54] observed that cyclohexane and methylcyclopentane are produced by heating hexane at 120° C. under pressure with the chloride.

Transformation of cyclohexane to methylcyclopentane derivatives, as well as dehydrogenation of cyclopentane derivatives, has been noted in other instances. Unger[55] reported that acetyl chloride reacts with cyclohexane in the presence of aluminum chloride to yield derivatives of methylcyclopentane and methylcyclopentene. According to Nenitzescu and Cantuniari,[56] methylcyclopentane, under the same conditions, forms 2-acetyl-1-methylcyclopentane and 2-acetyl-1-methylcyclopentene. The formation of the unsaturated ketone was shown to result from the presence of water in the aluminum chloride. During the reaction between cyclohexane and acetyl chloride, some acetaldehyde is produced. The hydrogen required for the reduction of acid chloride to the aldehyde is apparently derived from the saturated ketone formed by the reaction of cyclohexane and acetyl chloride. Another instance of a similar reduction is that occurring when 2-acetyl-1-methylcyclopentane dissolved in cyclohexane is treated with benzoyl chloride and aluminum chloride. No reaction was detected between the cyclopentane derivative and benzoyl chloride which was reduced to benzaldehyde with the simultaneous formation of an equivalent quantity of the hydrocarbon $C_{12}H_{22}$ from the cyclohexane.

Nenitzescu and Cantuniari[57] observed that when cyclohexane is boiled for several hours with anhydrous aluminum chloride, it is practically unchanged, but under the influence of aluminum chloride containing water it is converted largely into methylcyclopentane. The maximum yield is about 20 per cent. The same equilibrium can be reached by starting with methylcyclopentane. No evidence of the formation of dimethylbutane was obtained.

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[46] *Bull. soc. chim.*, 1916, **19**, 326; *Chem. Soc. Abs.*, 1916, **110** (1), 785.

[47] Nash and Mason (*Ind. Eng. Chem.*, 1934, **26**, 45) reviewed the action of halogens and halogen compounds, particularly aluminum chloride, on the heat treatment of hydrocarbons.

[48] *J. Russ. Phys.-Chem. Soc.*, 1892, **24**, 309; *Chem. Soc. Abs.*, 1893, **64** (1), 382.

[49] *Ann.*, 1873, **169**, 147; *Ber.*, 1873, **6**, 561; *Chem. Soc. Abs.*, 1873, **26**, 873.

[50] Hofmann, Otto, and Stegemann, U. S. Patent 1,885,060, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 1006.

[51] *Brennstoff-Chem.*, 1927, **8**, 321; *Brit. Chem. Abs.* **B**, 1927, 930.

[52] "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, 1932, 102.

[53] *Bull. soc. chim.*, 1925, **37**, 1549; *Chem. Abs.*, 1926, **20**, 899.

[54] *Z. angew. Chem.*, 1921, **34**, 406; *Chem. Abs.*, 1921, **15**, 4006.

[55] *Ber.*, 1932, **65**, 467. *Cf.* Hopff, *Ber.*, 1931, **64**, 2739.

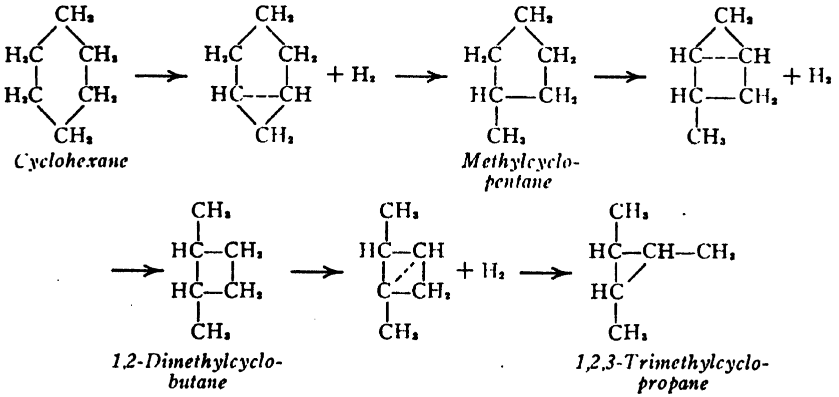
[56] *Ber.*, 1932, **65**, 1449.

[57] *Ber.*, 1933, **66**, 1097.

Zelinsky and Tarassova[58] pointed out that the isomerization of cyclohexane to methylcyclopentane does not take place quantitatively during the Friedel-Crafts reaction, but rather that its extent depends upon the experimental conditions. Furthermore, the production of unsaturated ketones by the reaction between acetyl chloride and cyclohexane is diminished by using an excess of aluminum chloride. In other words, an excess of aluminum chloride restricts the dehydrogenation of cyclohexane. The use of a poisoned catalyst (for example, technical aluminum chloride containing 3 per cent ferric chloride) increases the proportion of unsaturated ketones formed. The hydrogen liberated during the dehydrogenation reaction reduces the acid chloride to the aldehyde.

An unusual molecular rearrangement was observed by Hopff.[59] When cyclohexane is treated with carbon monoxide in the presence of aluminum chloride hexahydrobenzaldehyde is not formed but 1-methyl-2-cyclohexanone. Here no contraction of the ring takes place but rather a migration of a group from the nucleus to form a side chain.

Treatment of cyclohexane with aluminum chloride or bromide followed by dehydrogenation over a platinized carbon catalyst yielded methylcyclopentane, benzene, and dimethylcyclobutane. Aluminum bromide was found to dehydrogenate the latter compound to 1,2-dimethyldicyclo-[0,1,1]-butane, to which hydrogen adds yielding 1,2,3-trimethylcyclopropane.[60] These various steps, beginning with cyclohexane, may be illustrated as follows:



Zelinsky and Smirnov[61] noted that the decomposition of heptanaphthene (isolated from petroleum) by aluminum chloride in the presence of hydrochloric acid resulted in the formation of isobutane and an aluminum chloride-hydrocarbon complex $AlCl_3 \cdot C_4H_8$.

From their work on the decomposition of Galician, Austrian, American and Caucasian heavy oils by anhydrous aluminum chloride, Pictet and Lerczynska[62] concluded that side chains split off from naphthenic hydrocarbons with formation of a paraffin and the unsaturated cyclic residue polymerizes. This conclusion was substantiated by the comprehensive work of Grignard and Stratford.[63] These latter workers found that, by heating at 120° to 150° C. in the presence of 20 to 30 per cent of aluminum chloride, cyclohexane and methylcyclohexane are not changed, but both 1,2- and 1,4-dimethylcyclohexanes are isomerized to the 1,3-compound, the 1,4-compound isomerizing more readily. Derivatives of cyclohexane with side chains of 2 or 3 carbon atoms are converted by isomerization chiefly into the 3-methyl derivatives. For example, 1,3-diethylcyclohexane yielded largely tetramethylcyclohexane and only small quantities of butane. The three isomeric butylcyclohexanes form paraffins to the extent of 13 to 15 per cent, the products being n-butane from the normal and secondary isomers and a mixture of n- and isobutanes from tertiary butylcyclohexane. The principal reaction is an isomerization to a mixture of tetramethylcyclohexanes. Amyl- and isoamylcyclohexanes are decomposed to the extent of 70 per cent and 42 per cent, respectively, both yielding butane. Isomerization also occurs to form a mixture of tetramethyl- and pentamethylcyclohexanes.

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[58] *Ber.*, 1932, 65, 1249.

[59] *Ber.*, 1932, 65, 482.

[60] Zelinsky and Turova-Pollak, *Ber.*, 1932, 65, 1171.

[61] *Brennstoff-Chem.*, 1925, 6, 249; *Chem. Soc. Abs.*, 1925, 128 (1), 1125.

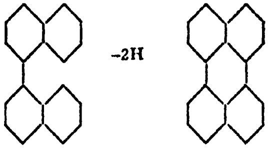
[62] *Bull. soc. chim.*, 1916, 19, 326; *Chem. Soc. Abs.*, 1916, 110 (1), 785.

It appears, therefore, that cyclohexane, cyclopentane and their immediate homologues are fairly stable toward anhydrous aluminum chloride. Cyclohexane and its derivatives, however, oftentimes undergo molecular rearrangement or dehydrogenation. Derivatives of the naphthene hydrocarbons, particularly those with long side chains, tend to split off the side chains with the formation of lower paraffin hydrocarbons (and subsequent polymerization of the unsaturated cyclic residue), or to isomerize to other polymethylene derivatives.

ACTION OF ALUMINUM CHLORIDE ON AROMATIC HYDROCARBONS

The most important reaction of aluminum chloride with aromatic hydrocarbons yields polynuclear hydrocarbons by dehydrogenation. This dehydrogenating action is facilitated by substances capable of taking up hydrogen.[64] Friedel and Crafts[65] found that at 180° C. in the presence of aluminum chloride benzene yields diphenyl, toluene and ethylbenzene, together with some ditolyl. As shown by Homer,[66] these changes take place even more readily with naphthalene, which yields dinaphthyl and higher hydrocarbons.

The condensation of higher aromatic hydrocarbons to produce others containing a larger number of aromatic nuclei also takes place under the influence of aluminum chloride. Scholl and his collaborators,[67] who paid particular attention to the use of aluminum chloride in the production of polynuclear aromatic substances, found that dinaphthyl could be readily converted into perylene,



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[63] *Compt. rend.*, 1924, 178, 2149; *Chem. Soc. Abs.*, 1924, 126 (1), 841.

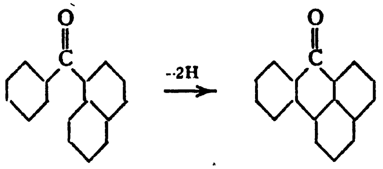
[64] Kränzlein, "Aluminumchlorid in der organischen Chemie," Verlag Chemie, Berlin, 1932, 79.

[65] *Compt. rend.*, 1885, 100, 692; *Chem. Soc. Abs.*, 1885, 48, 654. See also Anschütz and Immendorf, *Ber.*, 1885, 18, 657; *Chem. Soc. Abs.*, 1885, 48, 769.

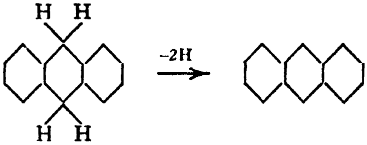
[66] *J.C.S.*, 1907, 91, 1103; *Chem. Abs.*, 1907, 1, 1551.

[67] Scholl, Seer and Weitzenböck, *Ber.*, 1910, 43, 2202; *Chem. Soc. Abs.*, 1910, 98 (1), 616.

and that phenyl-α-ketonaphthalene was dehydrogenated at 140° C. to yield benzanthrone[68];



Aluminum chloride can also act as a dehydrogenating agent without effecting nuclear condensation. For example, Scholl and Seer[69] have shown that it is possible to obtain anthracene by treating 9,10-dihydroanthracene with aluminum chloride.



A similar dehydrogenation of 9,10-diphenyl-9,10-dihydroanthracene to 9,10-diphenylanthracene has also been shown to take place.[70]

Besides these dehydrogenation reactions, aluminum chloride also causes a rearrangement and splitting off of side chains in certain benzene derivatives. Thus Copisarow[71] observed that when commercial xylene is heated at its boiling point with 3 to 20 per cent of its weight of aluminum chloride about one-half of the xylene is recovered unchanged, toluene is obtained in a yield of about 20 per cent together with a small quantity of benzene, and about 30 per cent of the original xylene is converted into substances of higher boiling points, probably higher homologues of benzene. Lacourt[72] reported that at room temperatures p-ter-butyl-toluene reacts with anhydrous aluminum chloride yielding isobutane, toluene, di- and tri-butyltoluene, some unchanged hydrocarbon and a high-boiling residue. Under the same conditions p-cymene yields benzene, toluene, xylene, 3,5-diisopropyltoluene, unchanged cymene and a high-boiling residue.

INDUSTRIAL APPLICATIONS OF THE POLYMERIZATION OF OLEFINS BY ALUMINUM CHLORIDE AND OTHER HALIDES

Much attention is being directed toward the polymerization of the very abundant supplies of olefins, particularly the gaseous ones, to high molecular weight hydrocarbons, especially with a view to producing synthetic lubricating oils.[73] Otto[74] found, for example, that the oils produced by the action of boron trifluoride on ethylene under pressure have lubricating properties. The work of Stanley (already discussed) on the production of oils from the polymerization of ethylene by anhydrous aluminum chloride is of interest in this connection.

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[68] Scholl and Seer, *Monatshefte,* 1912, **33**, 1; *Chem. Soc. Abs.,* 1912, **102** (1), 271; *Ann.,* 1912, **394**, 111; *Chem. Soc. Abs.,* 1913, **104** (1), 56.

[69] *Ber.,* 1922, **55**, 330; *Chem. Abs.,* 1922, **16**, 2505.

[70] Barnett, Cook and Nixon, *J.C.S.,* 1927, 504.

[71] *J.C.S.,* 1921, **119**, 1806.

[72] *Bull. soc. chim. Belg.,* 1929, **38**, 1; *Chem. Abs.,* 1929, **23**, 2431.

[73] See Nash, *J. Inst. Fuel,* 1930, **3**, 347. Petrov, *Khim. Tverdogo Topliva,* 1931, **2**, No. 11-12, 108-20. Progress in the manufacture of synthetic lubricating oils has been reviewed by Nash, *J. Inst. Pet. Tech.,* 1930, **16**, 313.

[74] *Brennstoff-Chem.,* 1927, **8**, 321; *Chem. Abs.,* 1928, **22**, 1465. This subject is treated in Chapter 26.

Brownlee[75] produced a low cold-test lubricating oil (pour test, —68° F.) by the polymerization of the liquid olefins in cracked gasolines with anhydrous aluminum chloride. A similar process was proposed by the Braunkohlen Produkte A.-G.[76] Gaseous olefins may also be polymerized by passing them under slight pressure through a suspension of aluminum chloride in gasoline or some other liquid medium at ordinary temperatures.[77] Krauch[78] reported that when gaseous olefins are passed into suspensions of aluminum chloride in petroleum ether polymerization to lubricant hydrocarbons of high molecular weight takes place. When the middle oils are used as the medium, not only do polymerization reactions occur but there is also a condensation between the middle-oil hydrocarbons and the olefins. The result is that from the thin middle oil, highly viscous oils somewhat similar in properties to lubricating oils derived from natural petroleum are produced.

The production of lubricating oils by the polymerization of olefins, particularly those from the cracking of paraffin wax, was described by Sullivan, Voorhees, Neeley and Shankland.[79] Such oils are characterized by high flash point, high specific gravity, relatively small changes in viscosity with temperature, excellent color, low Conradson carbon, and low susceptibility to oxidation. Furthermore, since no wax-like substances are formed during the polymerization process these oils also possess low pour tests. The method[80] of producing such oils may be described briefly as follows: The crude wax is cracked at atmospheric pressure at a temperature of 950° to 1000° F. (510° to 540° C.). A distillate having an end point of about 500° F. (260° C.) is separated from the products of cracking and this is polymerized by stirring with aluminum chloride (50 grams per gallon of distillate) for 18 hours at 210° F. (99° C.). The stirring is then stopped and the tar which settles is withdrawn. The remaining oil is next steamed until the desired viscosity is reached. In one example, the products so obtained consisted of about 10 per cent of light distillate, 80 per cent of an oil of 90 seconds Saybolt viscosity (at 210° F.), and about 10 per cent of tar.

Zherdeva[80a] treated cracked fractions boiling between 150° and 280° C. with 3 per cent aluminum chloride for 30 hours at 60° to 70° C. under atmospheric pressure. Two layers were formed, the upper containing a synthetic oil (amounting to 30 to 40 per cent) of low pour point and good viscosity index. On oxidation with air at 150° C. for 24 hours, carboxylic acids formed.

The products obtained by cracking mineral oils or tars, brown-coal tar oils or petroleum residues may be polymerized in the presence of anhydrous halides, such as aluminum chloride or boron fluoride, to yield lubricating oils.[81] The cracking operation can take place in the presence of metallic catalysts[82] (e.g., porous iron or nickel), or decomposition may be accomplished by first forming the chlorine derivatives of the hydrocarbons and then eliminating hydrogen chloride from these by heating in the presence of aluminum oxide, zinc chloride, or other similar catalysts.[83] Before condensation with aluminum chloride, aromatic hydrocarbons (naphthalene or anthracene) can be mixed with the products described above.

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[75] British Patent 141,753, 1920; *Chem. Abs.*, 1920, **14**, 2549; U. S. Patent 1,374,277, Apr. 12. 1921; *Chem. Abs.*, 1921, **15**, 2682; *Nat. Pet. News*, 1919, **9**, 35. *Cf.* U. S. Patent 1,309,432, July 8, 1919; *Chem. Abs.*, 1919, **13**, 2274.

[76] French Patent 608,425, 1925; *Brit. Chem. Abs.* **B**, 1927, 245.

[77] Soc. Ricard, Allenet et Cie. (Soc. anon. des. distilleries des Deux-Sèvres), British Patent 202,311, 1923; *Chem. Abs.*, 1924, **18**, 275. U. S. Patent 1,745,028, Jan. 28, 1930; *Brit. Chem. Abs.* **B**, 1930, 276.

[78] *Proc. Second Inter. Conference Bituminous Coal*, 1928, **1**, 32; *Oil & Gas J.*, 1929, **27**, 156, 158, 160; *Chem. Abs.*, 1929, **23**, 2284. See I. G. Farbenind. A.-G., British Patent 275,664, 1926; *Chem. Abs.*, 1928, **22**, 2463; Krauch and Müller-Cunradi, Canadian Patent 278,741, 1928; *Chem. Abs.*, 1928, **22**, 2829.

[79] *Ind. Eng. Chem.*, 1931, **23**, 604. This article gives a very complete account of methods for the polymerization of ethylene. See also Sullivan, Voorhees, Oak and Barnard, *J. Soc. Automotive Engrs.*, 1931, **29**, 40; *Chem. Abs.*, 1932, **26**, 5409.

[80] Sullivan and Voorhees, Canadian Patent 319,995, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, **26**, 2586. British Patent 355,214, 1929; *Chem. Abs.*, 1932, **26**, 4169. French Patent 690,966, 1930; *Chem. Abs.*, 1931, **25**, 1376.

[80a] *Neft. Khoz.*, 1932, **24**, 236; *Chem. Abs.*, 1933, **27**, 5177.

[81] I. G. Farbenindustrie A.-G., German Patent 540,014, 1927; French Patents 712,912, 1931; 713,149 and 713,150, 1931; *Chem. Abs.*, 1932, **26**, 1770.

[82] I. G. Farbenindustrie A.-G., British Patent 354,441, 1930.

In producing lubricating oils by the polymerization of olefins, the addition of finely divided aluminum, or zinc [84] or nickel [85] to the aluminum chloride, according to Howes, increases its activity. Hagemann [86] reported that the activity of the catalyst is reduced by the presence of oxygen or sulphur compounds.

Weizmann and Legg [87] proposed to polymerize butylene at a temperature of —10° C. in the presence of a catalyst such as aluminum chloride to form naphthene hydrocarbons in quantitative yields. It has also been stated that unsaturated hydrocarbons (isobutylene and amylene) can be polymerized by subjecting them to the action of the addition compounds of aluminum chloride, or other metallic chlorides, and substances other than olefinic hydrocarbons. Examples of such addition compounds are those of aluminum chloride with nitrobenzene, acetone and benzoyl chloride.[88] Haeuber [89] polymerized liquid olefins by heating them in the presence of the addition compound of ethylene and aluminum chloride, prepared by leading ethylene through a suspension of aluminum chloride in a saturated hydrocarbon at 40° to 60° C.

When gases rich in lower olefins such as ethylene, propylene, butylene and amylene, are passed into liquid hydrocarbons containing catalysts of the Friedel-Crafts type (aluminum, zinc, or ferric chlorides), oils which may be used as lubricants are obtained. The activity of the catalysts may be increased by the addition of mercuric or uranyl chloride. Temperatures up to 200° C. are recommended and either atmospheric or higher pressures may be employed.[90] According to Petrov, Antzus and Pozhiltzeva,[91] synthetic lubricating oils from cracking gas and aluminum chloride contain a smaller amount of aromatics when the reaction temperature is low. They also find that the synthetic oils are more homogeneous than natural mineral oils.

The polymerization of mineral and tar oils free from paraffin wax and boiling from 200° C. to 300° C. has been carried out by heating them below cracking temperatures in the presence of anhydrous aluminum chloride and finely divided metals or metalloids. For example, brown-coal tar (100 parts), having a viscosity of 2.8° Engler at 20° C., is stirred with 9 parts of aluminum chloride and 1 part of zinc dust at 180° C. for 8 hours. Copious evolution of hydrogen sulphide takes place but there is no cracking. Lubricating oil (46 per cent by weight) of a viscosity of 24° Engler at 20° C. together with burning oils is obtained.[92] Unsaturated oils from sulphur dioxide extracts of hydrocarbon oils may be polymerized with aluminum chloride below 150° C.[93]

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[83] I. G. Farbenindustrie A.-G., British Patent 363,823, 1930.

[84] British Patent 363,846, 1931; assigned to Imperial Chemical Industries, Ltd.

[85] British Patent 372,763, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 715. See also I. G. Farbenindustrie A.-G., British Patent 318,311, 1928; *Brit. Chem. Abs.* **B**, 1929, 883.

[86] *Erdöl u. Teer,* 1931, **7**, 464, 478; *Chem. Abs.,* 1932, **26**, 2583.

[87] U. S. Patent 1,395,620, Nov. 1, 1921; *J.S.C.I.*, 1921, **40**, 903A; British Patent 165,452, 1916; *J.S.C.I.*, 1921, **40**, 675A.

[88] Bataafsche Petroleum Maatschappij, British Patent 358,068, 1930. French Patent 716,159, 1931; *Chem. Abs.*, 1932, **26**, 2197. See also I. G. Farbenindustrie A.-G., British Patent 358,495, 1930; *Chem. Abs.*, 1932, **26**, 4945; British Patent 316,701, 1928; *Brit. Chem. Abs.* **B**, 1929, 932. Michel, Pungs and Galle, German Patent 548,578, 1927; *Chem. Abs.*, 1932, **26**, 4168.

[89] German Patent 557,305, 1929; assigned to I. G. Farbenindustrie, A.-G.; *Chem. Abs.*, 1933, **27**, 304.

[90] I. G. Farbenindustrie A.-G., British Patent 299,086, 1927; *Brit. Chem. Abs.* **B**, 1928, 919. Also French Patent 650,799, 1928; *Chem. Abs.*, 1929, **23**, 3341. British Patent 366,502, 1930; *Chem. Abs.*, 1933, **27**, 2030. French Patent 669,793, 1929; *Chem. Abs.*, 1930, **24**, 1970. French Patent 743,531, 1933; *Chem. Abs.*, 1933, **27**, 3812.

[91] *J. Applied Chem.* (*U.S.S.R.*), 1932, **5**, 790; *Chem. Abs.*, 1933, **27**, 186; *Refiner*, 1933, **12**, 293. See also I. G. Farbenindustrie A.-G., British Patent 320,846, 1928; *Brit. Chem. Abs.* **B**, 1930, 180.

Another process for converting mixtures of hydrocarbons (from the destructive hydrogenation of coal, the cracking of oils, or the low-temperature carbonization of coal) into products of higher boiling points consists of subjecting them to the action of a halogen, or halogen-exchanging substance, and a halide of an element from the third to eighth group of the periodic table.[94] The operation is generally conducted at a temperature below 100° C. As an example, 10 parts of middle oil, with a boiling range of 200° to 270° C., are treated with 1 to 2 parts of chlorinated methanes and 1 part of aluminum chloride at a temperature below 40° C. in a diluent such as benzene. According to a process developed by Chappell,[95] hydrocarbon oils containing naphthenes may be condensed with chlorinated gaseous hydrocarbons in the presence of aluminum chloride. The products are drawn into a second reaction zone where they are treated with more aluminum chloride at a higher temperature; decomposition into gasoline and high-boiling oil is said to take place. A viscous lubricating oil (yield 50 to 60 per cent) can be produced from paraffin wax or hydrocarbons having a mean molecular weight of 170 to 250 in the presence of aluminum chloride and agents such as chlorine, oxygen and sulphur.[96]

According to Thomas and Carmody,[97] who were especially interested in synthetic resins from petroleum hydrocarbons, four reactions appear to take place when a cracked petroleum distillate is treated with aluminum chloride:

(1) Reaction of olefins to form high-boiling oily polymers.
(2) Reaction of olefins with aromatics to form substituted aromatics.
(3) Polymerization of diolefins and olefins to form resins.
(4) Reaction of diolefins with substituted aromatics to form resins.

Reaction 1, while of importance in the production of lubricating oils, is detrimental to resin formation. Such oils, because of their high boiling points, are difficult to separate from the resin, and their presence in the resin reduces its melting point. Such low-melting resins are not generally desirable in the paint and varnish industry.

Reaction 2 does not stop with the monosubstituted compound, and di- and trisubstitutions often take place. These latter substituted aromatics are often high-boiling oils, and therefore the same objections are applicable to them as to the oils resulting from reaction 1.

With reference to reaction 3, Thomas and Carmody[98] have shown that when a pure diolefin is treated with aluminum chloride no apparent reaction takes place, but the addition of an olefin initiates it. For example, isoprene alone does not react with aluminum chloride, but when 2-pentene is added a violent reaction takes place. The reaction can be controlled by adding aluminum chloride slowly until it is complete. Breaking down the aluminum complex yields two polymers, one soluble and the other insoluble in hydrocarbon solvents. The proportion of the soluble polymer formed is a function of the amount of 2-pentene present, and the hardness of the resin varies inversely with this component. The insoluble polymer, having an empirical formula of C_5H_8, begins to depolymerize at about 116° C., is decomposed by strong acids and gives reddish-violet colorations with phenols.

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[92] I. G. Farbenindustrie A.-G., British Patent 318,311, 1928; *Brit. Chem. Abs.* **B**, 1929, 883.

[93] Halloran and Chappell, U. S. Patent 1,893,774, Jan. 10, 1933; assigned to Standard Oil Co. of California.

[94] I. G. Farbenindustrie A.-G., British Patent 320,846, 1928; *Brit. Chem. Abs.* **B**, 1930, 180.

[95] U. S. Patent 1,878,262, Sept. 9, 1932; *Brit. Chem. Abs.* **B**, 1933, 614; U. S. Patent 1,891,619, Dec. 20, 1932; *Brit. Chem. Abs.* **B**, 1933, 740; both patents assigned to Standard Oil Co. of California.

[96] I. G. Farbenindustrie A.-G., British Patent 349,071, 1930; *Brit. Chem. Abs.* **B**, 1931, 832. See also French Patent 669,518, 1929, *Chem. Abs.*, 1930, **24**, 1970; and British Patent 322,284, 1928; *Brit. Chem. Abs.* **B**, 1930, 94.

[97] *Ind. Eng. Chem.*, 1932, **24**, 1125.

[98] *J.A.C.S.*, 1932, **54**, 2480.

Diolefins react with substituted benzenes (reaction 4) to yield hydrocarbon resins. This reaction is governed both by the number of substituting groups in the benzene nucleus and by their nature. Thus, isoprene reacts very slowly, if at all, with benzene, but much more rapidly with toluene and with xylene. With the three xylenes, the yield of resin is less with the p-compound than with o-xylene; m-xylene is intermediate. Again, when the benzene nucleus contains a substituent group other than methyl, the yield of resin is the greater and its color the lighter, the larger and more branched the group.

Cyclic olefins (which react much more vigorously to yield a harder resin of better character) and diolefins follow the same general course of reaction as their corresponding straight-chain homologues.

Chapter 7

Production of Hydrogen and Carbon by Pyrolysis of Hydrocarbons

The pyrolysis of all hydrocarbons leads ultimately to their resolution into carbon and hydrogen.[1] Methane is the most resistant of all hydrocarbons to heat[2] and is always the most important final product (together with carbon and hydrogen) of their thermal treatment. In the initial stages of heating, each hydrocarbon follows its own individual decomposition reactions, but the final result is always the same, namely, the production of carbon, hydrogen and methane in proportions which gradually approach the equilibrium concentrations at the particular temperature used of the reaction $CH_4 \rightleftarrows C + 2H_2$. The dissociation is endothermic and, accordingly, the extent of decomposition increases rapidly with rise in temperature. The equilibrium concentrations of this reaction have been determined (see Chapter 2) and at atmospheric pressure and various temperatures in the presence of nickel are given in Table 45[3]:

TABLE 45.—*Decomposition of Methane:* $CH_4 \longrightarrow C + 2H_2$.

Temp. ° C.	CH_4	H_2	Temp. ° C.	CH_4	H_2
	—Per Cent—			—Per Cent—	
500	53.4	46.6	900	3.4	96.6
600	29.9	70.1	1000	1.8	98.2
700	14.5	85.5	1100	1.0	99.0
800	6.8	93.2	1200	0.6	99.4

Bone and Coward[4] showed that methane differs from other hydrocarbons in that its decomposition is a surface phenomenon even at temperatures of 1200° C. and probably above, whereas with ethane, ethylene and other hydrocarbons the decomposition takes place throughout the whole mass of gas. However, even under favorable conditions, the rate of decomposition of methane is very slow, Pring[5] finding that heating for 22 hours at 1200° C. or 2 hours at 1500° C. was necessary in order to attain equilibrium in this reaction. The experimental results of Holliday and Exell,[6] on the dissociation of methane at various pressures and temperatures up to 1200° C., suggest a reaction approaching equilibrium but bearing no relation to the true reversible equilibrium. They thought this apparent equilibrium resulted from the deposition not of pure carbon but of a hydrocarbon possessing a vapor pressure greater than that of carbon. Holliday and Exell noticed, as have many other observers, that nickel increases the velocity of reaction enormously.

[1] Marchand, *J. pr. Chem.*, 1846, **36**, 478. See Bone and Coward, *J.C.S.*, 1908, **93**, 1197.

[2] See Francis, *Ind. Eng. Chem.*, 1928, **20**, 277. von Wartenberg, *Z. physik. Chem.*, 1907, **61**, 366; *Chem. Soc. Abs.*, 1908, **94** (2), 26; *Z. physik. Chem.*, 1908, **63**, 269; *Chem. Soc. Abs.*, 1908, **94** (2), 676.

[3] Scheffer, Dokkum and Al, *Rec. trav. chim.*, 1926, **45**, 803.

[4] *J.C.S.*, 1908, **93**, 1197; see Chapter 2.

[5] *J.C.S.*, 1910, **97**, 498.

[6] *J.C.S.*, 1929, 1066.

The various processes for the production of carbon and hydrogen from hydrocarbons differ from one another considerably, the conditions being dependent on the character of the products desired. The carbon initially formed in the pyrolysis of hydrocarbons is converted into the amorphous gray variety if subjected to high temperatures for too long a time.[7] Because of this it is necessary to use various devices to remove the carbon promptly from the reaction zone if carbon black, lampblack and similar types of carbon are the desired products. Moreover, in the production of carbon black it is probably best to employ fairly low temperatures. When harder and coarser forms of carbon are desired, one may use high temperatures and fairly long heating periods, that is, conditions which secure optimum yields of hydrogen from simple thermal decomposition processes.

Various materials (metallic iron, nickel and cobalt) are known to catalyze the formation of carbon and hydrogen in the pyrolysis of hydrocarbons, but, in actual operation, the surfaces of the catalyst soon become covered with a layer of carbon which inhibits the catalytic action.[8] Unless means are provided for removing the carbon deposit, either blowing it out at high gas speeds or burning it off periodically with a current of air or oxygen, the catalyst tends to become ineffective. Much attention has been directed to certain other processes which are capable of being catalyzed efficiently but in which the activity of the contact materials is not vitiated by carbon deposition. Among these are the reactions of methane with steam or carbon dioxide:

$$\begin{aligned} CH_4 + H_2O &\longrightarrow CO + 3H_2 \\ CH_4 + 2H_2O &\longrightarrow CO_2 + 4H_2 \\ CH_4 + CO_2 &\longrightarrow 2CO + 2H_2 \end{aligned}$$

and the partial catalytic oxidation of methane with oxygen at high temperatures:

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2$$

These reactions are discussed fully later (Chapter 10) but it is well to note that they all yield mixtures of hydrogen and oxides of carbon and that the quantity of hydrogen produced by the introduction of steam is greater than that obtained in purely thermal decomposition processes. The manufacture of carbon and hydrogen by the direct pyrolysis of hydrocarbons only is considered in this chapter.

The conditions necessary for the production of relatively high grade carbons appear to be (1) comparatively low temperatures consistent, of course, with sufficient rate of decomposition, but, more particularly, (2) the rapid removal of the carbon from the hot reaction zone before it is converted into the hard gray amorphous variety. The carbon formed in some of the earlier thermal processes was almost valueless, the hydrogen being usually the product desired. For example, in one commercial installation for the thermal decomposition of natural gas, only hydrogen was collected. The carbon black simultaneously produced was grayish in color, contained hard particles, had a high apparent specific gravity, and had only one-fifth the tinting strength of ordinary carbon black. Naphthalene was also present in some samples, thus impairing its utility in the rubber-tire industry. The product found no market although some application was made of it in the formulation of cheap paints.[9]

The very low yields of carbon black (corresponding to about 5 per cent of the total carbon) from its manufacture by the incomplete combustion of natural gas (see Chapter 8) have focussed attention on other possible methods of production. The earlier processes proposed for the thermal decomposition of natural gas were unsuccessful, even though yields as high as 40 per cent of the theoretical carbon were obtained, because of the inferior quality of the product.[10] Since 1922 this difficulty has been overcome to a great extent and carbon blacks made in this way have won a place in the market. The thermal decomposition processes not only yield an increased proportion of carbon but simultaneously produce hydrogen. From 1000 cubic feet of methane it is theoretically possible to obtain 31.82 pounds of carbon and 2000 cubic feet of hydrogen.[11] In one process (Thermatomic), a yield of 7 pounds of carbon is obtained consistently from every thousand cubic feet of natural gas.[12] Most of the early processes described in this chapter appear to have been designed primarily for the production of hydrogen, although it is conceivable that some of them might be modified to yield carbon for special purposes.

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[7] Perrott, *U. S. Bur. Mines Bull.*, 192, 1922, 59.

[8] Holliday and Exell, *loc. cit.*; Chamberlin and Bloom, *Ind. Eng. Chem.*, 1929, 21, 945; Wheeler and Wood, *Fuel*, 1928, 7, 535. See Chapter 2.

[9] Neal and Perrott, *U. S. Bur. Mines Bull.* 192, 1922.

Production of Carbon and Hydrogen by Simple Thermal Decomposition

In 1886 McTighe[13] proposed a method for the production of carbon by passing hydrocarbon vapors through a heated retort and separating the carbon in depositing chambers. Later, Purtle and Rowland[14] passed hydrocarbon gases at a pressure of 10 pounds per square inch into a closed retort heated to 800° C. and periodically removed the deposited carbon by means of a scraper.

By decomposing hydrocarbon gas in a retort heated electrically at 1300° to 1800° C. and depositing the liberated carbon on the bottom of the retort, which is maintained at a relatively lower temperature, Snee[15] prevented the coking of the carbon which would otherwise occur at the temperature of decomposition.

To avoid the presence of such impurities as naphthalene, Fernekes[16] produced lampblack from methane or natural gas by passing the gas through an alundum tube heated to a temperature of 1300° to 1700° C. Under these conditions the gas is decomposed into carbon and hydrogen without the formation of intermediate products.

Szarvasy[17] described a process for the production of pure retort carbon by passing methane over pieces of carbon heated to a glowing temperature in an inclined retort. The carbon forms a dense and strongly adherent deposit on the carbon fragments. The carbon particles, whose size is thus increased, are removed either intermittently or continuously, and smaller fresh carbon fragments are introduced to replace them. The heating is effected electrically, or by combustion of methane-air or hydrogen-air mixtures. The heating by combustion and the decomposition reaction may be effected alternately in separate stages in the same retort.

By passing methane through an externally heated chamber composed of previously formed carbon, or carbon fragments, Szarvasy[18] also obtained carbon. Since the incandescent walls of the carbon reaction chamber are efficient surfaces for promoting the dissociation of the methane, carbon-fragment filling may be omitted. As the decomposition proceeds the carbon must be removed periodically, together with the original carbon walls which must be replaced. Part of the resulting material may be used for relining the decomposition chambers and part for the manufacture of carbon electrodes.[19]

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[10] See Neal and Perrott, *U. S. Bur. Mines Bull.* **192**, 1922.

[11] Moore, *Ind. Eng. Chem.*, 1932, **24**, 21.

[12] *Chem. Met. Eng.*, 1932, **39**, 380.

[13] U. S. Patents 346,168 and 346,169, July 27, 1886; Neal and Perrott, *U. S. Bur. Mines Bull.* **192**, 1922.

[14] U. S. Patent 866,883, Sept. 24, 1907; *J.S.C.I.*, 1907, **26**, 1151.

[15] U. S. Patents 1,036,362 and 1,036,363, Aug. 20, 1912; *J.S.C.I.*, 1912, **31**, 885.

[16] U. S. Patent 1,066,894, July 8, 1913; assigned to Snee; *Chem. Abs.*, 1913, **7**, 3016.

[17] U. S. Patent 1,199,220, Sept. 26, 1916; *Chem. Abs.*, 1916, **10**, 2983.

[18] U. S. Patent 1,392,266, Sept. 27, 1921; *Chem. Abs.*, 1922, **16**, 336. *Cf.* British Patents 158,888, 158,889 and 158,891, 1921; *Chem. Abs.*, 1921, **15**, 1974; British Patent 159,823, addition to 158,891, 1921; *Chem. Abs.*, 1921, **15**, 2174.

By using a mixture of nitrogen and methane in such an operation it is possible to obtain a mixture of hydrogen and nitrogen for the synthesis of ammonia.[20]

Szarvasy and Bensel[21] suggested making soot carbon, retort graphite and similar products from natural gas by continuously passing the gas through a heated retort. A yield of 65 per cent carbon is thus obtained and the hydrogen produced simultaneously can be used for heating the retort or for other purposes. Szarvasy[22] also proposed conducting natural gas or other hydrocarbon gas into a chamber maintained at a temperature at which decomposition of the gas occurs. The reaction chamber has walls with holes blocked by a porous carbon deposit or other pervious material and is heated, at least in part, by combustible gases passing through the walls and burning in immediate proximity to them.

Bunte[23] investigated the decomposition of coal gas by passing it through porcelain tubes, both unpacked and packed with iron filings or coke. The gas produced at a temperature of 1100° to 1200° C. had no illuminating value but showed an increased volume and higher hydrogen content. The laboratory studies of Bunte were later extended by von Oechelhaeuser[24] to the production of the so-called "Dessau balloon gas," containing 80.7 to 84.1 per cent hydrogen, 5 to 7 per cent methane, 5.1 per cent nitrogen, and 7.3 per cent carbon monoxide. For this purpose he passed coal gas at 1200° C. over finely granulated coke in common horizontal gas retorts. The carbon produced simultaneously was obtained in two forms, as a finely divided carbon black and as silver-gray crystalline needles.

The Rincker-Wolter Process.

Rincker and Wolter[25] produced hydrogen from oils and tars by thermal decomposition in two generators, somewhat resembling water-gas generators, charged with coke and arranged either one above the other or side by side. After the first generator is heated to incandescence by an air blast, tar is introduced and partly converted into gas by contact with the glowing coke. This gas escapes by expansion. A current of air is then introduced and carries the remaining tar vapors into the second generator where more complete gasification takes place. At the same time this air blow raises the coke in the first generator to incandescence. The process is then reversed; tar is introduced into the second generator and the tar vapors and gas are carried with the blast of air into the first generator.

For hydrogen production by this process the coke bed must be maintained at a temperature of about 1200° C., since too low a temperature yields a gas so poor in hydrogen that subsequent purification is not commercially feasible. At the end of the blowing run, oil is sprayed onto the hot coke for several minutes and this is followed by a current of steam to clear the sprayer. The gases formed by the decomposition pass through water seals to scrubbers and purifiers. By careful working it is possible to obtain a gas containing 96 per cent hydrogen, 1.3 per cent nitrogen, and 2.7 per cent carbon monoxide. The nitrogen content is somewhat reduced by passing this gas over heated soda-lime.[26] To avoid clinkering of the ash of the fuel, Ellis [27] proposed the addition of a small proportion of lime to the coke to flux the ash and thus maintain the requisite fuel-bed temperature.

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[19] The manufacture of carbon .electrodes is described by Szarvasy in U. S. Patent 1,392,267, Sept. 27, 1921; *Chem. Abs.*, 1922, 16, 336; British Patent 158,890, 1921; *Chem. Abs.*, 1921, 15, 1860.

[20] Szarvasy, U. S. Patent 1,417,952, May 30, 1922; *Chem. Abs.*, 1922, 16, 2759.

[21] U. S. Patent 1,398,751, Nov. 29, 1921; *Chem. Abs.*, 1922, 16, 823.

[22] U. S. Patent 1,592,474, July 13, 1926; *Chem. Abs.*, 1926, 20, 3216.

[23] *J. Gasbel.*, 1894, 37, 81; *J.S.C.I.*, 1894, 13, 933; *Chem. Zentr.*, 1894, 1, 610.

[24] *J. Gasbel.*, 1909, 52, 883; *Chem. Zentr.*, 1909, 2, 1905; *J. Gasbel.*, 1910, 53, 693; *Chem. Zentr.*, 1910, 2, 930.

[25] French Patent 346,092, 1904; *Chem. Abs.* 1907, 1, 130. German Patent 174,253, 1904; *Chem. Abs.*, 1907, 1, 1198; British Patent 10,422, 1908; *Chem. Abs.*, 1909, 3, 2501; British Patent 16,027, 1908; *Chem. Abs.*, 1910, 4, 105; German Patent 223,148, 1908; *Chem. Abs.*, 1910, 4, 3134; Canadian Patent 131,747, 1911; *Chem. Abs.*, 1911, 5, 1992. French Patents 391,867 and 391,868, 1908; *J.S.C.I.*, 1908, 27, 1144.

In a modification of the Rincker-Wolter process,[28] the conversion of liquid hydrocarbons into oil gas is effected by contact with glowing coal or coke in the normal way, and gases containing hydrogen (water gas) are introduced into the oil-gas generator to convert the oil residues into gasified hydrocarbons. This also avoids the formation of tar in the oil-gas generator. Two units are employed, functioning as water-gas generator and oil-gas generator, alternately. A portable plant of the Rincker-Wolter type mounted on two ordinary railway flat cars was used for the production of hydrogen for military purposes.[29] Processes similar to the Rincker-Wolter have been described by Frasch,[30] Lowe,[31] and Thorssell.[32]

Geisenberger [33] generated hydrogen by decomposing low-boiling hydrocarbons such as benzine or other organic materials (bitumen, shale, beeswax, or turpentine) with heat.

Brunner [34] described a process in which natural gas, crude petroleum or garbage grease was converted into hydrogen by passing the gas through a furnace and then through a series of vertical standpipes (connected at top and bottom) through which water is sprayed to remove carbon and other impurities.

A gas of high hydrogen content has been produced by the Berlin-Anhaltische Maschinenbau-A.-G. [35] from coal gas by a process similar to the Rincker-Wolter. Illuminating gas is first freed from carbon dioxide and is then conducted over white-hot coke, yielding a mixture consisting almost entirely of hydrogen, carbon monoxide and nitrogen. The carbon monoxide is removed by treatment with soda-lime and the resulting hydrogen-nitrogen mixture is said to be well adapted for many technical purposes. This process was the subject of exhaustive tests carried out by Weaver.[36] The method, as before stated, consists essentially of a decomposition of hydrocarbon oil by passage of the vapors over surfaces sufficiently hot to decompose the hydrocarbons completely into their elements. In carrying this out a blast of air is blown through a bed of coke to heat it to incandescence in the usual way. The resulting "blast gas" is then burned in a tower filled with checkerbrick, called the vaporizer. When both coke and brick have attained the desired temperature, the oil is vaporized and the resulting vapors are allowed to pass first through the column of brick and then through the hot coke. The carbon deposited in both chambers is burned out during the next air blow and provides part of the fuel necessary for maintaining the required temperature.

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[26] See Taylor, "Industrial Hydrogen," Chemical Catalog Co., Inc., New York, 1921, 154.

[27] U. S. Patent 1,092,903, April 14, 1914; *J.S.C.I.*, 1914, **33**, 550.

[28] Hollandsche Residugas Maatschappij Systeem Rincker-Wolter, British Patent 6,285, 1915; *J.S.C.I.*, 1916, **35**, 625; Norwegian Patent 27,930, 1917; *Chem. Abs.*, 1917, **11**, 2729; Dutch Patent 2,655, 1918; *Chem. Abs.*, 1919, **13**, 904; French Patent 478,836, 1916; *Chem. Abs.*, 1916, **10**, 2297; Swiss Patent 72,359, 1915; *Chem. Abs.*, 1916, **10**, 2635. *Cf.* Rincker, British Patent 139,451, 1919; *Chem. Abs.*, 1920, **14**, 2077; U. S. Patent 1,388,145, Aug. 16, 1921; *Chem. Abs.*, 1921, **15**, 4046; Canadian Patent 181,962, 1918; *Chem. Abs.*, 1918, **12**, 763.

[29] Scientific American Supplement, Sept. 5, 1914, 155.

[30] U. S. Patent 1,118,899, Nov. 24, 1914; *J.S.C.I.*, 1915, **34**, 19.

[31] U. S. Patent 1,174,511, Mar. 7, 1916; *Chem. Abs.*, 1916, **10**, 1424.

[32] British Patent 288,154, 1928; *Brit. Chem. Abs.* **B**, 1929, 719. British Patent 298,190, 1928; *Brit. Chem. Abs.* **B**, 1930, 143.

[33] French Patent 361,492, 1905; *J.S.C.I.*, 1906, **25**, 885. Steam may also be used in this process. See Chapter 10.

[34] U. S. Patent 1,246,867, Nov. 20, 1917; *Chem. Abs.*, 1918, **12**, 297.

[35] German Patent 267,944, 1913; *Chem. Abs.*, 1914, **8**, 1663; *J.S.C.I.*, 1914, **33**, 190. French Patent 466,040, 1913; British Patent 2,054, 1914; *J.S.C.I.*, 1914, **33**, 783. *Cf.* French Patent 465,575, 1913; *Chem. Abs.*, 1914, **8**, 3491; and British Patent 28,390, 1913; *J.S.C.I.*, 1914, **33**, 256. Sander, *Z. angew. Chem.*, 1912, **25**, 2401. This article gives a comprehensive discussion of the methods of producing hydrogen down to that time. See also *Chem. Met. Eng.*, 1911, **9**, 157.

[36] *Chem. Met. Eng.*, 1923, **28**, 764, 939, 1072; *Chem. Abs.*, 1923, **17**, 2173, 2477, 2768.

In preparing hydrogen from crude petroleum or petroleum tar oils, Pictet [37] proposed to heat the vapors in such a manner that 18.1 calories are supplied to each 16 grams of gas passed through a tube at a temperature of 1200° to 1350° C. Similarly, hydrocarbons such as petroleum vapors mixed with steam may be converted into a mixture of carbon monoxide and hydrogen.[38] By admitting a regulated quantity of oxygen, Pictet [39] found that its combination with the hydrocarbon material can likewise be made to yield sufficient heat to carry on the reaction.

Nauss [40] proposed to obtain hydrogen from coal gas by first converting its carbon monoxide content into methane by catalytic reduction and then subjecting the resulting gas to decomposition at 1000° to 1200° C. in retorts containing coke, charcoal, or clay, impregnated with nickel, cobalt or iron.

The Thermatomic Process.

Undoubtedly the most important of the methods developed for making carbon black by thermal decomposition is the so-called Thermatomic process,[41] the basic ideas of which have been described by Brownlee and Uhlinger.[42] The process consists in heating a furnace lined with refractory brick and filled with checkerbrick to incandescence by an upward blast of natural gas and air, shutting off the air and allowing the natural gas (admitted from the top at this stage), to decompose. The intermittent heating and cracking processes (the latter being endothermic) are carried out alternately. Approximately two-thirds of the total quantity of carbon black produced is formed by impingement against the refrac-

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[37] British Patent 13,397, 1911; *Chem. Abs.*, 1912, 6, 3515. German Patent 257,715, 1910; *Chem. Abs.*, 1913, 7, 2470.

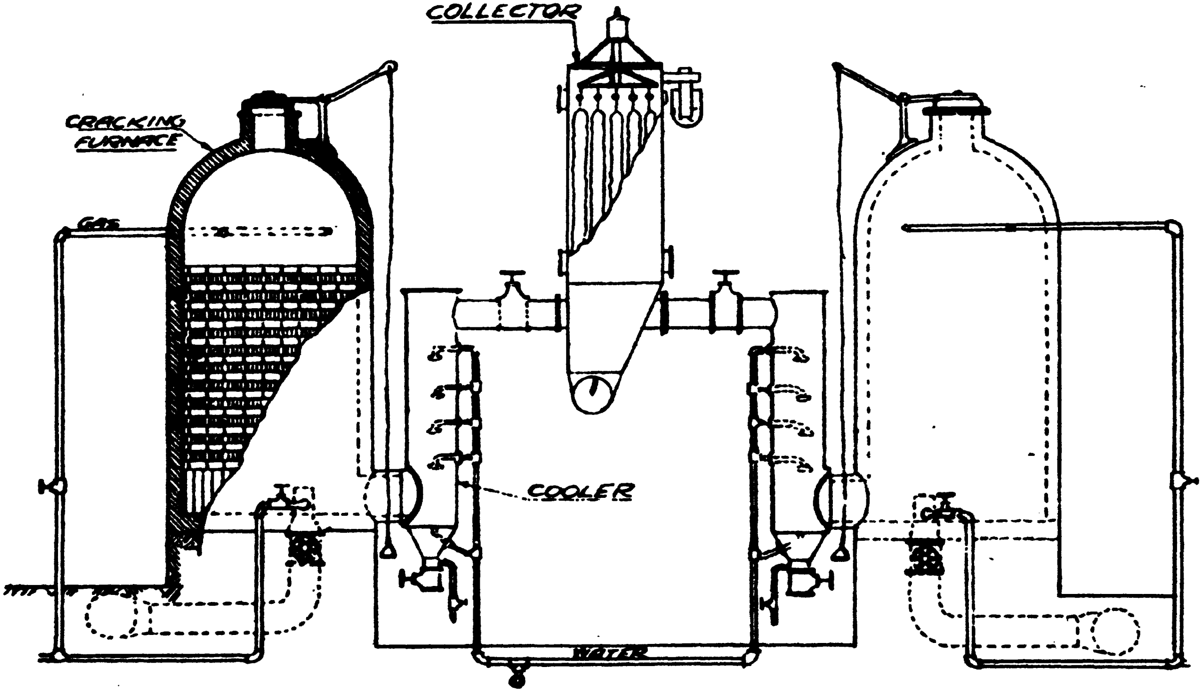
[38] Pictet, British Patent 14,703, 1911; *Chem. Abs.*, 1913, 7, 244. See also Chapter 10.

[39] Pictet, British Patent 16,373, 1911; *Chem. Abs.*, 1913, 7, 245. *Cf.* British Patent 24,374, 1913; *Chem. Abs.*, 1915, 9, 1242; U. S. Patent 1,134,416, April 6, 1915; *Chem. Abs.*, 1915, 9, 1374; German Patent 289,065, 1912; *Chem. Abs.*, 1916, 10, 2508.

[40] U. S. Patent 965,482, July 26, 1910; *Chem. Abs.*, 1910, 4, 2728; German Patent 226,609, 1909; *Chem. Abs.*, 1911, 5, 1333; British Patent 2,298, 1910; *Chem. Abs.*, 1911, 5, 2313.

[41] This process has been commercially exploited by the Thermatomic Carbon Co. of Pittsburgh, Pa., and a plant has been in operation at Sterlington, La. See *Chem. Met. Eng.*, 1932, 39, 380; and Moore, *Ind. Eng. Chem.*, 1932, 24, 21.

[42] Canadian Patent 158,273, 1914; *Chem. Abs.*, 1915, 9, 516; U. S. Patent 1,168,931, Jan. 18, 1916; assigned to American Nitro-Products Co.; *Chem. Abs.*, 1916, 10, 811; British Patent 5,098, 1915; *Chem. Abs.*, 1916, 10, 2393; U. S. Patent 1,265,043, May 7, 1918; *Chem. Abs.*, 1918, 12, 1691; U. S. Patent 1,276,487, Aug. 20, 1918; assigned to American Nitro-Products Co.; *Chem. Abs.*, 1918, 12, 2114; U. S. Patent 1,478,730, Dec. 25, 1923; *Chem. Abs.*, 1924, 18, 735. Canadian Patent 242,163, 1924; *Chem. Abs.*, 1924, 18, 3689; U. S. Patent 1,520,115, Dec. 23, 1924; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1925, 19, 710; Uhlinger, U. S. Patent 1,363,488, Dec. 28, 1920; *Chem. Abs.*, 1921, 15, 737; U. S. Patents 1,707,775, April 2, 1929, and 1,718,720, June 25, 1929; both assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1929, 23, 4029; Canadian Patents 285,031 and 285,032, 1928; both assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1929, 23, 940. See also Spear and Moore, British Patent 307,743, 1928; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1930, 24, 212; Canadian Patent 271,013, 1927; *Chem. Abs.*, 1927, 21, 3430; U. S. Patent 1,794,558, March 3, 1931; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1931, 25, 2331. Spear, Canadian Patent 264,324, 1926; *Chem. Abs.*, 1926, 20, 3697; Canadian Patent 304,622, 1930; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1930, 24, 5950. U. S. Patent 1,880,512, Oct. 4, 1932; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1933, 27, 574. Miller, U. S. Patent 1,857,469, May 10, 1932; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1932, 26, 3884. U. S. Patent 1,881,325, Oct. 4, 1932; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1933, 27, 574. Boardman, U. S. Patent 1,710,469, April 3, 1929; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1929, 23, 2608. U. S. Patent 1,638,421, Aug. 9, 1927.



Courtesy Industrial and Engineering Chemistry.

FIG. 19.—General Arrangement of Plant for Thermal Decomposition of Hydrocarbons. (Thermatomic Process.)

tory material or comes into contact with it after formation. Such carbon is valueless commercially and is left in the furnace to be consumed in the next air blow. It is stated[43] that the most desirable operating temperature for the cracking process is 1200° to 1400° C. and the mixture of hydrocarbon and resulting gases, together with the carbon produced, is subjected to these temperatures for a period of 3 to 4 seconds only.

On issuing rapidly from the furnace, the mixture of gases and carbon is passed through a cooling chamber where just enough water is sprayed countercurrent to the gas stream[44] to cool the smoke to a safe temperature for filtering through cloth bags without leaving an excess to wet either the bags or the carbon. The appended diagram (Fig. 19), which is largely self-explanatory, shows the form of apparatus which has been developed, consisting essentially of two cracking furnaces, two coolers, and one collector. Moore[45] gave the typical analyses shown in Table 46 of the natural gas being used and the resultant gas obtained in this process:

TABLE 46.—*Thermatomic Process Gas Analyses, Per Cent by Volume.*

	Natural Gas	Resultant Gas
Carbon dioxide	0.4	0.9
Illuminants	0.7	1.3
Hydrogen	—	85.4
Carbon monoxide	—	1.1
Methane	93.8	5.0
Nitrogen	5.1	6.3

This process has been producing the carbon called "Thermax" since 1922. Another brand, called "P-33," which is blacker and finer than Thermax and was put on the market later, is made in the same way as Thermax, except that a portion of the resulting gas is recirculated and acts as a diluent for the decomposing natural gas. This dilution principle is so effective that it reduces the average particle size to about one-fifth that of Thermax.[46] A comparison of the physical and chemical properties of these two carbons, as reported by Moore,[47] is given in Table 47.

TABLE 47.—*Properties of Thermatomic Carbons.*

	Thermax	P-33
Specific gravity	1.80	1.80
Apparent gravity (kg./cu. meter)	481.5	356.1
Tinting strength[a]	14%	50%
Average particle size	1.0 micron	0.23 micron
Moisture	0.25%	0.25%
Ash	0.05%	0.15%
Benzene extract (16 hrs. extraction)	0.60%	1.25%

[a] The standard for these tinting strength percentages was Cabot's channel black.

Passing natural gas, previously freed from hydrogen sulphide, through a furnace filled with incandescent coke or refractory material for the production of hydrogen was proposed by Frank.[48] The decomposition of the gas begins at

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[43] Brownlee and Uhlinger, U. S. Patent 1,478,730, Dec. 25, 1923.

[44] Brownlee and Uhlinger, U. S. Patent 1,520,115, Dec. 23, 1924; assigned to Thermatomic Carbon Co.

[45] *Ind. Eng. Chem.*, 1932, 24, 21.

[46] Spear and Moore, Canadian Patent 271,013, 1927; *Chem. Abs.*, 1927, 21, 3430; U. S. Patent 1,794,558, March 3, 1931; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1931, 25, 2331. British Patent 307,743, 1928; assigned to Thermatomic Carbon Co.; *Chem. Abs.*, 1930, 24, 212.

[47] *Loc. cit.*

[48] U. S. Patent 1,107,926, Aug. 18, 1914; *Chem. Abs.*, 1914, 8, 3359. See Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930, 768.

800° C. but complete decomposition into its elements is not obtained below 1200° C. In a similar way Rose[49] prepared a gas containing as much as 98 per cent of hydrogen by conducting natural gas or oil vapors over refractory materials heated to 1650° C.[50] Herman[51] produced soot and hydrogen from light hydrocarbons, especially natural gas, by contact with highly heated refractory surfaces against which the gas is allowed to impinge in a number of finely divided currents. Pyzel[51a] substantially confines the decomposition to fractions heavier than methane by regulating the rate of gas flow and the temperature of the refractory material. The resulting gas is purified and fractionated, the undesired compounds obtained thereby being used to heat the refractory material. The heat of the cracked products is also utilized by injecting into the hot gas stream at various points, further quantities of the gas to be treated.[51b]

The process of Bacon, Brooks and Clark[52] for the production of carbon black and practically pure hydrogen from hydrocarbons was devised to insure a satisfactory yield of both products in continuous operation. It is conducted in such a manner that the particles of carbon black remain suspended in the hydrogen and are thus rapidly removed from the reaction zone, thereby avoiding deterioration of the carbon from continued heat treatment. The temperature of decomposition is maintained above 1200° C. and the rate of feed of the hydrocarbon is so adjusted that the gas velocity developed is sufficient to sweep the carbon particles from the reaction zone. Substantially pure hydrogen is obtained and the recovered carbon black has a silky luster.

Ellis[53] has described a furnace connected to a brick checkerwork chamber which may be used for the thermal treatment of hydrocarbons to yield hydrogen. Hydrocarbon oil is introduced above a bed of coke heated to a white heat and the resulting vapors are passed through the heated checkerwork where further decomposition occurs. The furnace is provided with air and steam inlet pipes for blowing up the fire and for sweeping out the gases.

In another process McCourt and Ellis[54] obtained carbon and hydrogen by forcing methane through a highly heated porous bed of refractory material at such a speed that the carbon particles are removed from the hot reaction zone.

To produce hydrogen Barth[55] decomposed liquid fuels (oils or tars) in a furnace and subjected the gaseous products of the decomposition to a further thermal treatment in a separate furnace. It is stated that by this method of operation, there is an economical use of fuel and the contact mass on which hydrogen formation proceeds does not become contaminated with carbon. The furnace or vaporization chamber is an iron jacket lined with firebrick and filled with a refractory grating or with coarse pieces of refractory material. The combustion gases escaping from the generator during the blow-period are passed through the refractory grating of the vaporization chamber. Near the end of the blow-period the gas contains carbon monoxide and this is burned within the vaporization chamber after the admission of air. In this way the heat necessary for vaporizing the liquid fuel is provided. After the air supply is shut off, the vaporized oil is passed into the vaporization chamber and thence through the glowing charge of coke in the generator. The coke is maintained at about 1000° C. if illuminating gas is to be made, but a higher temperature is necessary for the production of hydrogen. The oil vapors are passed through the generator alternately in opposite directions, that is, first from above and then from below.

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[49] U. S. Patent 1,254,360, Jan. 22, 1918; *Chem. Abs.*, 1918, **12**, 760; *cf.* U. S. Patent 1,230,226, June 19, 1917; *Chem. Abs.*, 1917, **11**, 2271.

[50] See also Compagnie nationale de matières colorantes et manufactures de produits chimiques (Établissements Kuhlmann), British Patent 286,291, 1927; *Chem. Abs.*, 1929, **23**, 246.

[51] German Patent 290,883, 1914; *Chem. Abs.*, 1917, **11**, 883.

[51a] U. S. Patent 1,896,420, Feb. 7, 1933; assigned to Shell Development Co.; *Chem. Abs.*, 1933, **27**, 2769.

[51b] Pyzel, British Patent 391,532, 1933; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 4910.

[52] U. S. Patent 1,220,391, Mar. 27, 1917; *Chem. Abs.*, 1917, **11**, 1733. See Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930, 765.

[53] U. S. Patent 1,092,903, April 14, 1914; *Chem. Abs.*, 1914, **8**, 2038.

[54] U. S. Patent 1,276,385, Aug. 20, 1918; *Chem. Abs.*, 1918, **12**, 2114; McCourt, Canadian Patent 187,661, 1918; *Chem. Abs.*, 1919, **13**, 169.

[55] U. S. Patent 1,172,925, Feb. 22, 1916; *Chem. Abs.*, 1916, **10**, 1091.

Snelling[56] proposed to heat organic compounds capable of reversible thermal dissociation in a closed chamber, the walls of which are more permeable to hydrogen than to other substances. The hydrogen formed is withdrawn through the permeable walls during the reaction. Battig[57] produced hydrogen from methane or other hydrocarbons by passing them successively through a preheated chamber containing a latticework of bricks, an apparatus heated to the temperature necessary for decomposition, a chamber in which carbon is deposited, and a cooling chamber also packed with bricks. When the last chamber becomes unduly heated, the supply of gas is shut off and air or oxygen is passed through the apparatus in the reverse direction to burn away the carbon and to reheat the preheating chamber. The carbon may be deposited on coke, iron, or on ores for subsequent smelting. Steam and oxygen may also be used in the decomposition to produce carbon dioxide and hydrogen.[58] A similar process has been described by Vinther.[59] The carbon which deposits on the refractory during the decomposition is burned to carbon monoxide, which is then burned to preheat a second chamber, thus rendering the process cyclic and independent of an external fuel supply.

Nelson[60] proposed to make refined lampblack by decomposing hydrocarbon oils at 500° to 700° C. in the absence of air. The liberated carbon is collected in a condensing chamber (maintained at 400° C.) and the gases pass on and are condensed, the non-condensible substances being used later to heat the apparatus. To remove the last traces of volatile matter from the carbon a current of hot gas (e.g., that obtained in the process) may be passed over it.

Burwell[61] described the production of hydrogen and carbon of good quality by the thermal decomposition of hydrocarbons. In his process a stream of natural gas or vaporized petroleum hydrocarbon preheated to a temperature just short of decomposition (about 150° to 450° C.) is mixed with a diluent (hydrogen) heated to 1200° to 1300° C. This mixture is allowed to remain in a heated zone until substantially complete decomposition of the hydrocarbon material is effected. The products are then passed to a cool settling chamber where the carbon separates. The resulting gas, consisting largely of hydrogen, is divided into two portions, the major portion being retained in the closed circuit (i.e., used as a gaseous diluent for further decomposition of hydrocarbon material), and the remainder withdrawn for purification. By varying the hydrocarbon raw material and the ratio of the gaseous diluent to gaseous decomposition products in the mixture, the quality of the carbon produced can be changed. A similar process has been proposed by Day.[62] Burwell[63] obtained hydrogen containing 0.2 per cent methane and 0.7 per cent carbon monoxide by passing a hydrocarbon oil through two retorts, the first heated at 950° to 1000° C., and the second at 1140° to 1170° C., with settling chambers after each for the removal of carbon black. A similar method of using two heating chambers with one expansion chamber was proposed by Fischer[64] for the manufacture of lampblack.

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[56] U. S. Patent 1,124,347, Jan. 12, 1915; *J.S.C.I.*, 1915, **34**, 249. *Cf.* U. S. Patent 1,596,070, Aug. 17, 1926; *Chem. Abs.*, 1926, **20**, 3337.

[57] British Patents 271,483 and 271,491, 1926; *Chem. Abs.*, 1928, **22**, 1658; French Patent 634,711, 1927; *Chem. Abs.*, 1928, **22**, 3980; French Patent 635,670, 1927; *Chem. Abs.*, 1928, **22**, 4737; Canadian Patent 284,117, 1928; *Chem. Abs.*, 1929, **23**, 677. U. S. Patent 1,726,877, Sept. 3, 1929; *Chem. Abs.*, 1929, **23**, 5282. *Cf.* U. S. Patent 1,831,943, Nov. 17, 1931; assigned to Patentverwertungs A.-G. "Alpina"; *Chem. Abs.*, 1932, **26**, 813; French Patent 698,484, 1930; *Chem. Abs.*, 1931, **25**, 3136.

[58] Battig, British Patent 294,113, 1927; *Chem. Abs.*, 1929, **23**, 1999. French Patent 35,613, 1928, addition to French Patent 634,716; *Chem. Abs.*, 1930, **24**, 4125.

[59] U. S. Patent 1,817,726, Aug. 4, 1931; *Brit. Chem. Abs.* **B**, 1932, 466.

[60] British Patent 172,035, 1920; *J.S.C.I.*, 1922, 41, 65A.

[61] U. S. Patent 1,717,354, June 18, 1929; assigned to Alox Chemical Corporation; *Chem. Abs.*, 1929, **23**, 4060. See also Miller, U. S. Patent 1,857,469, Oct. 15, 1932; assigned to Thermatomic Carbon Co.; *Brit. Chem. Abs.* **B**, 1933, 339.

Finely divided carbon and a mixture of hydrogen and nitrogen in the ratio of 3 to 1 are obtained by Wilcox[64a] in the following manner. An active combustion of fuel gas takes place in the retort. The fuel gas passes countercurrent to the hydrocarbon gas and air, maintaining thereby a temperature of about 1100° C. The nitrogen and hydrogen produced may be used in the synthesis of ammonia. In Burke's[64b] method for the production of carbon black, gaseous hydrocarbons diffuse into a stream of highly heated gas. The flow of gas is maintained in a non-turbulent stream. Preheated natural gas may be subjected first to a cracking temperature and the cracked stock passed through a series of chambers.[64c] Each of these chambers has a temperature lower than the cracking temperature and contains cool hydrogen. The gas thus undergoes a "shocking" treatment, carbon black being recovered from the "shocked" stock.

On passing methane preheated to 800° C. through a vertical graphite or carborundum tube, Padovani[64d] obtained higher hydrocarbons along with carbon and hydrogen. The tube was heated to 1000° to 1300° C., and was so dimensioned that the ratio of area of contact (square centimeters) to volume (cubic centimeters) was 0.25 to 1. The heating period was 0.5 to 6 seconds and the pressure was approximately 1 atmosphere.

The distribution of the products of the thermal decomposition of a hydrocarbon gas in a cool inert gas to collect and separate them was described by Lewis.[65]

A process for making carbon in which vapors of hydrocarbons are passed at such a rate through a bed of incandescent coke maintained at 1000° to 1200° C. that the gases emerge at a temperature of 600° to 700° C., has also been suggested.[66] The carbon formed is swept out of the reaction chamber by the gaseous products.

In another process hydrocarbon vapors pass through a mass of ignited fuel and are converted into carbon, hydrogen and methane.[67] The temperature of the fuel is so regulated that the methane in the hydrocarbon gases, as well as that formed by decomposition of the higher hydrocarbons, is decomposed by contact with the surface of the fuel and all the carbon liberated is retained on the surfaces of the fuel. According to Perry,[68] the hydrocarbons may be separated from the gas and used again. The fuel bed may be treated with steam to decompose the deposited carbon with the production of water gas, from which more hydrogen is recoverable. The hydrocarbons and steam may also be passed through the fuel bed simultaneously.

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[62] U. S. Patent 1,804,249, May 5, 1931; *Brit. Chem. Abs.* **B**, 1932, 828; *Chem. Abs.*, 1931, **25**, 3781.

[63] U. S. Patent 1,819,732, Aug. 18, 1931; assigned to Alox Chemical Corporation; *Brit. Chem. Abs.* **B**, 1932, 492.

[64] U. S. Patent 1,528,324. March 3, 1925; *Chem. Abs.*, 1925, 19, 1477.

[64a] U. S. Patent 1,918,362, July 18, 1933; *Chem. Abs.*, 1933, **27**, 4889. U. S. Patent 1,892,862, Jan. 3, 1933; *Chem. Abs.*, 1933, **27**, 2255. See also Brownlee, U. S. Patent 1,920,352. Aug. 1, 1933; *Chem. Abs.*, 1933, **27**, 4889; U. S. Patent 1,909,163, May 16, 1933; *Chem. Abs.*, 1933, **27**, 3787.

[64b] U. S. Patent 1,902,797, Mar. 21, 1933; assigned to General Atlas Chemical Co.; *Chem. Abs.*, 1933, **27**, 3299.

[64c] Starr, U. S. Patent 1,903,247, Mar. 28, 1933; *Chem. Abs.*, 1933, **27**, 3321.

[64d] British Patent 395,893, 1932; *Brit. Chem. Abs.* **B**, 1933, 851.

[65] U. S. Patent 1,536,612, May 5, 1925; assigned to Goodyear Tire and Rubber Co.; *J.S.C.I.*, 1925, **44**, 557B.

[66] Soc. d'études et réalisation dite Eréal, British Patent 353,100, 1929; *Chem. Abs.*, 1932, **26**, 3632. *Cf.* British Patent 342,034, 1928; *Chem. Abs.*, 1931, **25**, 4369. See also Yunker, U. S. Patents 1,901,884, 1,901,885, and 1,902,746, Mar. 21, 1933; assigned to Natural Gas Hydrogen Corp.; *Chem. Abs.*, 1933, **27**, 3299.

[67] Humphreys and Glasgow, Ltd., French Patent 716,343, 1931; *Chem. Abs.*, 1932, **26**. 2305; Terzian, British Patent 365,912, 1931; assigned to Humphreys and Glasgow, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 298.

[68] British Patent 370,289, 1931; assigned to Humphreys and Glasgow, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 547; French Patent 722,627, 1931; *Chem. Abs.*, 1932, **26**, 4141; U. S. Patent 1,848,654, March 8, 1932; assigned to United Gas Improvement Co.; *Chem. Abs.*, 1932, **26**, 2832.

In the procedure developed by Hillhouse,[68a] a shower of incandescent carbon is allowed to fall through the gas. An axial flame is maintained in the chamber and serves to heat the carbon.

Lewis[69] obtained a mixture containing 15 to 70 per cent hydrogen by passing natural gas, stripped of its heavier constituents, through a tube heated at 600° to 900° C. At this temperature no free carbon is formed. The cyclic hydrocarbons produced in this pyrolysis may be removed by condensation. The gas may be burned to yield carbon black (see Chapter 8).

Garner[70] decomposes natural gas thermally to yield a gas of low calorific value and carbon black. For use as a fuel, the gas resulting from the decomposition is mixed with untreated natural gas in such proportions that the higher calorific value is obtained.

For drying carbon black, the use of the combustible gases formed in the pyrolysis has been suggested.[71]

Other processes for the decomposition of methane or natural gas have been developed by the Ruhrchemie A.-G. and by the Bataafsche Petroleum Maatschappij. In the former[72] the gas is heated at 900° to 1200° C., producing a gaseous mixture containing up to 60 per cent hydrogen which can be used for the autogeneous welding of metals. In the latter[73] the hydrocarbon mixture is heated in a vessel resembling a blast-furnace stove, and after cooling, the resulting gas is scrubbed to remove lampblack, tar, and naphthalene. The hydrogen can be separated from the other gaseous products (ethylene or propylene) by fractionation (see Chapter 4). The cracking of natural gas in water-gas generators to produce carbon black and gases rich in hydrogen was investigated by Odell.[74]

Carbon having the crystalline structure of graphite was obtained by Hofmann and Groll[75] by dropping benzene (boiling at 60° to 70° C.) from a capillary through a vertical quartz tube heated to 950° C.

Carbon and hydrocyanic acid, according to Poindexter,[76] are the products of heating a mixture of ammonia and natural gas, kerosene vapor or other hydrocarbon material.

DECOMPOSITION EFFECTED BY PARTIAL COMBUSTION OF HYDROCARBONS

In many of the methods thus far described, the heat required for the reaction is obtained from some external source or from an incandescent fuel bed and in others the temperature is maintained by combustion of the deposited carbon. The thermal conditions necessary for the decomposition may be secured by partial combustion of some of the hydrocarbon material itself, the basis of a number of processes. Carbon monoxide, one of the products of the combustion, is itself capable of decomposing or of burning to carbon dioxide and brief mention of a few processes in which this occurs is also included in the discussion. Another larger and better-known group of methods in which incomplete combustion of some of the hydrocarbon material maintains the decomposition temperature is discussed in Chapter 8, where deposition of carbon from flames is considered. This, too, is apparently a purely thermal decomposition induced by the heat of combustion of a portion of the hydrocarbon supply. It is perhaps well to anticipate also at this point two other means of maintaining the temperature required to effect decomposition which will be discussed later, namely, the electric arc and metallic baths maintained at high temperature.

[68a] U. S. Patent 1,892,559, Dec. 27, 1932; *Chem. Abs.*, 1933, **27**, 2284.

[69] British Patent 309,488, 1929; *Brit. Chem. Abs.* **B**, 1930, 936.

[70] U. S. Patent 1,767,357, June 24, 1930; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 191.

[71] Société l'air liquide (Soc. anon. pour l'étude et l'exploitation des procédés Georges Claude), French Patent 705,874, 1930; *Chem. Abs.*, 1932, **26**, 266.

[72] British Patent 350,413, 1928; *Chem. Abs.*, 1932, **26**, 2023.

[73] Dutch Patent 25,305, 1931; *Chem. Abs.*, 1932, **26**, 2023.

[74] *U. S. Bur. Mines, Rept. of Investigations* **2991**, 1930; *Chem. Abs.*, 1930, **24**, 2577.

[75] *Ber.*, 1932, **65**, 1257.

[76] U. S. Patent 1,562,914, Nov. 24, 1925; *Chem. Abs.*, 1926, **20**, 481.

Frost and Nix[77] proposed the manufacture of gases and carbon black by the incomplete combustion of petroleum vapor in a closed chamber. Darrah[78] introduced fuel oil into a current of heated gases containing insufficient oxygen for complete combustion to obtain a high grade lampblack. Poindexter,[79] to prepare a carbon pigment, heated natural gas to a temperature slightly below the point of decomposition and then mixed it with air at a higher temperature in an amount insufficient for complete combustion.

The oxidation of methane or its homologues with air or oxygen, and carbon dioxide has been used by Bradley[80] in making lampblack. The reacting gases are mixed in such proportions and at such temperatures, that enough additional heat is generated by the exothermic oxidation of the hydrocarbon to compensate for that consumed by the endothermic reaction of the carbon dioxide with the hydrocarbon. The carbon monoxide produced in the reaction is converted to carbon dioxide, which is then separated and utilized again. Goodwin[81] mixed air and a hydrocarbon gas or vapor in a reaction chamber, heated to a temperature above the maximum attainable by combustion of the mixture, to produce finely divided carbon. Lewis[81a] partially burned hydrocarbons and allowed the flames to impinge on metallic surfaces, obtaining a deposit of carbon black.

The reduction of carbon monoxide or dioxide by finely divided carbon has also been proposed as a method of manufacture of carbon black.[82]

A process of producing carbon black described by Matlock[83] consists in burning hydrocarbon gases in a furnace with a regulated supply of air. On passing upward through the furnace the gas and air mixture encounters a zone of burning gases. After cooling the resulting gaseous product, the carbon is separated. Bone[84] obtained hydrogen by using a proportion of oxygen or air with the hydrocarbon gas large enough to avoid deposition of carbon and passing the gaseous products over coke at a temperature of 1200° C. Steam may be added and austenitic steels or silica may be used for the apparatus. A similar process has also been proposed by the I. G. Farbenindustrie A.-G.[85]

Carbon monoxide has received some consideration as a possible source of finely divided carbon on account of the ease with which it decomposes into free carbon and carbon dioxide in the presence of metallic catalysts at temperatures of about 300° C. and over, according to the reaction:[86]

$$2CO \longrightarrow C + CO_2$$

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[77] British Patent 16,623, 1908; *Chem. Abs.*, 1909, **3**, 2501; U. S. Patent 977,000, Nov. 29, 1910; *Chem. Abs.*, 1911, **5**, 782.

[78] U. S. Patent 1,448,655, Mar. 13, 1923; *Chem. Abs.*, 1923, **17**, 1886.

[79] U. S. Patent 1,402,957, Jan. 10, 1922; *Chem. Abs.*, 1922, **16**, 1018.

[80] U. S. Patent 1,396,018, Nov. 8, 1921; *Chem. Abs.*, 1922, **16**, 618.

[81] U. S. Patent 1,758,152, May 13, 1930; assigned to Delano Land Co.; *Chem. Abs.*, 1930, **24**, 3331.

[81a] U. S. Patents 1,881,084 and 1,881,085, Oct. 4, 1930; *Brit. Chem. Abs.* **B**, 1933, 693.

[82] Tarup, Canadian Patent 175,937, 1917; see Perrott, *U. S. Bur. Mines Bull.* **192**, 1922.

[83] U. S. Patent 1,798,614, March 31, 1931; assigned to Monroe-Louisiana Carbon Co.; *Brit. Chem. Abs.* **B**. 1931, 1083.

[84] British Patent 349,471, 1930; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1932, **26**, 2023.

[85] British Patent 349,060, 1929; *Chem. Abs.*, 1932, **26**, 2023.

[86] See Deville, *Compt. rend.*, 1864, **59**, 873; *Compt. rend.*, 1865, **60**, 317; Bell, *J.C.S.*, 1869, **22**, 203. An excellent account of the decarbonization of carbon monoxide is given by Marek and Hahn, "Catalytic Oxidation of Organic Compounds in the Vapor Phase," Chemical Catalog Co., Inc., New York, 1932, 108.

Processes have been described for the production of a finely divided carbon by decomposing carbon monoxide at 600° to 1000° C. in the presence of iron or iron oxide.[87] Other catalysts (nickel or cobalt and their oxides) have also been proposed.[88] A vaporized carbonyl of a metal of the iron group was proposed as a catalyst for this reaction by Kramer and Bub[89] and by Haag.[90] The reaction is carried out at about 400° C. under 100 atmospheres pressure. Grosskinsky[91] prepared lampblack by splitting carbon monoxide or hydrocarbons using as catalysts, metals or oxides of the iron group obtained by decomposition of compounds other than their carbonyls.

DECOMPOSITION EFFECTED IN THE ELECTRIC ARC

The decomposition of gaseous and liquid hydrocarbons by the electric arc is discussed in Chapter 9. Several such methods, however, in which carbon and hydrogen are produced by the decomposition follow.

Winkler[92] observed the formation of carbon and non-condensible gases from heavy California oils by the action of an electric arc (Birkeland-Eyde) in hydrogen. By passing an electric arc between carbon electrodes immersed in various organic liquids contained in an ice-cooled flask, Tarczynski[93] obtained precipitated and colloidal carbon.

Hutchins[94] proposed a process in which a film of tar or oil on a revolving carbon or graphite disc is subjected to the action of one or more electric arcs in an air-tight casing. The gas and lampblack are drawn off through a pipe by a fan. The lampblack is separated by a filter and part of the gas is drawn off and part is returned for further treatment. Instead of the electric arc, one or more oxyhydrogen, oxyacetylene, or other high-temperature gas flames may be used.[95]

Jakowsky[96] made a study of electrical methods of manufacturing carbon black. Attempts to dissociate natural gas with various types of nitrogen-fixation apparatus ("spreading arc") were made, but the experiments indicated these methods to be impracticable. Both an intermittent and a continuous type apparatus, however, gave considerable proportions of carbon, which caused short-circuiting of the electrodes and lead-in tubes, as it formed in a fluffy deposit. By washing out the carbon with water or oil as formed, this difficulty was overcome and the apparatus thus modified worked satisfactorily in continuous operation.[97] The effects of pressure, enriching the gas with gasoline, use of high-frequency current, and passing the gas and arc through apertures in mica discs were investigated. The decomposition of liquid hydrocarbons was also effected in such an apparatus. Lower voltages and higher currents could be used with oil. It was found that oxygen compounds such as creosote broke down more easily than paraffins but they tended to form pitch and gummy residues. Carbon black obtained by such electrical processes compared favorably with the better grades of the commercial product both in tinting strength and particle size. Unlike ordinary commercial black, it does not tend to agglomerate when dispersed in oil. The non-condensible gases formed in the electrical production of carbon black from oils contain approximately 10 per cent methane, 50 per cent hydrogen and 35 per cent unsaturated hydrocarbons. The manufacture of alcohols from these unsaturated hydrocarbons (see Chapter 11) was considered. In their experiments on the decomposition of methane in the high-tension arc, Stanley and Nash [98] also obtained up to 20 per cent of finely divided carbon and a gas containing up to 14 per cent acetylene and 2 per cent ethylene.

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[87] J. G. Aarts, British Patent 246,130, 1925; *Chem. Abs.*, 1927, **21**, 488; H. C. J. Aarts, British Patent 278,745, 1926; assigned to General Carbonalpha Co.; *Chem. Abs.*, 1928, **22**, 2571; C. J. G. Aarts, British Patent 308,351, 1928; *Chem. Abs.*, 1930, **24**, 212; French Patent 671,488, 1929; *Chem. Abs.*, 1930, **24**, 2256; J. G. Aarts and H. C. J. Aarts, French Patent 674,545, 1929; assigned to General Carbonalpha Co.; *Chem. Abs.*, 1930, **24**, 2845. The use of this finely divided carbon as a fuel and a lubricant is described by J. G. Aarts in British Patent 246,132, 1925; *Chem. Abs.*, 1927, **21**, 488; German Patent 497,617, 1925; *Chem. Abs.*, 1930, **24**, 4140; German Patent 483,285, 1925; *Chem. Abs.*, 1930, **24**, 474.

[88] Dyche-Teague, British Patent 160,561, 1919; *Chem. Abs.*, 1921, **15**, 2342; British Patent 268,853, 1925; *Chem. Abs.*, 1928, **22**, 1498; U. S. Patent 1,670,599, May 22, 1928; *Chem. Abs.*, 1928, **22**, 2493. Ewan, British Patent 294,759, 1927; assigned to Cassel Cyanide Co., Ltd.; *Chem. Abs.*, 1929, **23**, 2000; British Patent 314,163, 1928; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1930, **24**, 1188. Schmidt, U. S. Patent 1,894,126, Jan. 10, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2540.

[89] U. S. Patent 1,803,855, May 5, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3781; *cf.* I. G. Farbenindustrie A.-G.; French Patent 700,252, 1930; *Chem. Abs.*, 1931, **25**, 3781; British Patent 286,845, 1927; *Brit. Chem. Abs.* **B**, 1928, 357; British Patent 319,140, 1928; *Brit. Chem. Abs.* **B**, 1929, 968.

[90] German Patent 540,864, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2285; *cf.* I. G. Farbenindustrie A.-G., French Patents 704,424 and 704,425, 1930; *Chem. Abs.*, 1931, **25**, 4671.

[91] German Patent 551,534, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 4924. *Cf.* I. G. Farbenindustrie A.-G.; British Patent 321,402, 1928; *Brit. Chem. Abs.* **B**, 1930, 90; British Patent 327,548, 1929; *Chem. Abs.*, 1930, **24**, 5117.

[92] *J. Franklin Inst.*, 1914, **178**, 97.

[93] *Z. Elektrochem.*, 1916, **22**, 252; *J.S.C.I.*, 1916, **35**, 889.

[94] U. S. Patent 1,309,070, July 8, 1919; *Chem. Abs.*, 1919, **13**, 2264. British Patent 124,557, 1918; *Chem. Abs.*, 1919, **13**, 1752.

[95] British Patent 126,560, 1918; addition to British Patent 124,557, 1918; *Chem. Abs.*, 1919, **13**, 2985.

[96] *U. S. Bur. Mines Techn. Paper* 351, 1924; *Chem. Abs.*, 1926, **20**, 1034.

Hydrogen is also produced by passing hydrocarbons through an electric arc. A gas containing 14 per cent methane and 86 per cent hydrogen, for example,[99] may be treated in this way to obtain a gas containing 7 per cent acetylene and 93 per cent hydrogen. Coke-oven or natural gas may be converted to a gas consisting almost entirely of hydrogen by a similar process.[100] Bethenod [101] effected decomposition by immersing high-fusing conductors heated to above 800° C. in the liquid under treatment. By this method, anthracene oil can be made to yield hydrogen and acetylene.

Eisenhut [102] proposed to make carbon, hydrogen, and acetylene by subjecting hydrocarbon vapors under pressure to the action of an electric arc at temperatures above 2500° C. Hydrocarbons such as methane are passed through the arc at such a rate that the ratio of the rate in cubic meters per hour to the power of the arc in kilowatts is below 0.6. The gases containing the soot can be directed into a cooled chamber and the lampblack separated by cooling in stages.[103]

Processes for the purification of carbon black generally involve heating the black to temperatures high enough to drive off volatile hydrocarbons. For example, the carbon obtained by the action of an electric arc on a hydrocarbon oil can be freed from water and unchanged oil by heating at 350° to 400° C., according to Gobert.[104]

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[97] Jakowsky, U. S. Patent 1,597,277, Aug. 24, 1926; *Chem. Abs.*, 1926, **20**, 3337.

[98] *J.S.C.I.*, 1929, **48**, 238T.

[99] I. G. Farbenindustrie A.-G., British Patent 286,845, 1927; *Chem. Abs.*, 1929, **23**, 488. Apparatus is described in British Patent 263,859, 1925; *Chem. Abs.*, 1928, **22**, 32.

[100] I. G. Farbenindustrie A.-G., British Patent 307,529, 1927; *Chem. Abs.*, 1929, **23**, 5282.

[101] British Patent 316,905, 1928; *Chem. Abs.*, 1930, **24**, 1806; French Patent 643,927, 1927; *Chem. Abs.*, 1929, **23**, 1740.

[102] German Patent 523,627, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3577; I. G. Farbenindustrie A.-G.; British Patent 336,261, 1930; *Brit. Chem. Abs.* **B**, 1931, 102.

[103] I. G. Farbenindustrie A.-G., French Patents 721,826 and 721,877, 1931; *Chem. Abs.*, 1932, **26**, 4142.

[104] British Patent 345,237, 1929; *Brit. Chem. Abs.* **B**, 1931, 526; *Chem. Abs.*, 1932, **26**, 266. See also Bosch, German Patent 271,901, 1913; *J.S.C.I.*, 1914, **33**, 557. Société l'air liquide (Soc. anon. pour l'étude et l'exploitation des Procédés Georges Claude), French Patent 705,874, 1930; *Chem. Abs.*, 1932, **26**, 266.

DECOMPOSITION EFFECTED IN BATHS OF MOLTEN METALS

Lampblack and hydrogen were obtained by Masson[105] by passing a combustible mixture of air and methane, or other hydrocarbons, through a bath of molten magnesium, copper, silver, nickel or slag maintained at a temperature of 1100° C. (2000° F.). In passing through the bath, the hydrocarbon is dissociated into its elements and the carbon as formed is blown out by the hydrogen. On leaving the bath, the reaction products are cooled as quickly as possible to 120° C. (250° F.) and the lampblack is precipitated, in order to produce a soft and fluffy product. The hydrogen can be used as a fuel to maintain the temperature of the bath. Paris,[106] on the other hand, suggested the use of a metal of lower melting point, such as lead. On leading the hydrocarbon vapors through the mass of molten lead the lampblack formed floats on the surface of the liquid and is removed by a stream of gas. Bähr[107] proposed the use of fused iron and fused copper at 1300° C. in a similar process.

For producing hydrogen, methane is blown into a bath of molten iron at a temperature of 1200° to 1300° C. in a method described by Tyrer.[108] The carbon liberated by the decomposition dissolves in the iron and is subsequently removed by blowing with air or a gas containing oxygen. Alternatively, the methane and air can be blown continuously into opposite ends of a reaction chamber provided with a partition dipping below the surface of the iron to prevent mixing of the gaseous products in the two sections. Additional air may be admitted above the iron in the oxidation section to oxidize the carbon monoxide formed. A catalyst (nickel) may be added to the iron bath, together with manganese to increase the solubility of the catalyst and the carbon in the iron. Steam may also be mixed with the methane.

CARBON AND HYDROGEN FROM ACETYLENE

The explosive nature of mixtures of air and hydrocarbons is well known.[109] Any mixture with air containing from 3 to 82 per cent of acetylene, for example, is explosive.[110] Most hydrocarbons require a high temperature for decomposition into carbon and hydrogen, as pointed out previously. This is because the dissociation reaction is endothermic, that is, non-explosive. However, acetylene is an exception. Heated at moderately high temperatures without oxygen it undergoes an exothermic (explosive) dissociation into carbon and hydrogen. Rimarski[111] found that pure acetylene decomposes spontaneously in the presence of iron surfaces heated to 510° C. at a pressure of 2.05 atmospheres. Below this temperature, even on raising the pressure, no indication of explosive decomposition was observed. The effect of other metals and metal powders in promoting this explosive decomposition was also studied by Rimarski and Konschak.[112] Acetylene is slowly decomposed at 180° C. by iron, cobalt, nickel and silver powders, and at 200° C. by copper powder. Copper decomposes acetylene with explosive violence at 460° C., but with ferric oxide, cupric oxide and manganese oxide (Mn_3O_4), the temperature need be no higher than 240° to 310° C. Such substances as aluminum oxide, silicon dioxide and active carbon also promote explosion at these temperatures.

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[105] U. S. Patent 1,418,385, June 6, 1922; *Chem. Abs.*, 1922, **16**, 2760.

[106] U. S. Patent 1,756,877, April 29, 1930; *Brit. Chem. Abs.* **B**, 1931, 189.

[107] German Patent 516,991, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3136.

[108] British Patent 328,048, 1929; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1930, **24**, 5117; and U. S. Patent 1,803,221, April 28, 1931; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 3781.

[109] See, for example, Jones, *U. S. Bur. Mines Tech. Paper* 450, 1929; *Chem. Abs.*, 1929, **23**, 4344; Jones and Perrott, *Quart. Nat. Fire Protect. Assoc.*, 1930, **23**, 385; *Chem. Abs.*, 1930, **24**, 6018. Von Schwartz, "Fire and Explosion Risks" (translated by Salter), Griffin and Co., London, 1904, 33. Vogel, "Das Acetylen, seine Eigenschaften, seine Herstellung, und Verwendung, Otto Spamer, Leipzig, 1925. See also Chapter 44.

[110] See, for example, Bunte, *Ber.*, 1898, **31**, 5; Clowes, *Proc. Chem. Soc.*, 1895, 201; 1896, 143; Berthelot and Vieille, *Compt. rend.*, 1896, **123**, 523; *Chem. Soc. Abs.*, 1897, **72** (2), 91; *Compt. rend.*, 1897, **124**, 988; Claude, *Compt. rend.*, 1899, **128**, 303; *Chem. Soc. Abs.*, 1899, **76** (1), 397; Mixter, *Am. J. Sci.*, 1900, **9**, 1; *Chem. Soc. Abs.*, 1900, **78** (1), 197; *Am. J. Sci.*, 1900, (4) **10**, 299; *Chem. Soc. Abs.*, 1900, **78** (1), 618.

[111] *Autogene Metallbearbeitung*, 1929, **22** (10), 130; *Acetylen in Wiss. u. Ind.*, 1929, **32** (5), 69; *Chem. Abs.*, 1929, **23**, 4344.

The decomposition of hydrocarbons, especially acetylene, with or without air, has been used to make a special quality of carbon black. This black, usually referred to as acetylene black, is very soft and fluffy and has an inherent bluish tinge which makes it desirable for some purposes.[113] Refuse calcium carbide, such as a grade too finely divided or having too low a content of carbide to be marketable, is a source of acetylene for conversion to this by-product black. Neal[114] stated that a carbon made by burning acetylene (see Chapter 8) is of better color than that made by explosion.[114a]

Hubou[115] produced acetylene black and hydrogen by exploding acetylene in a closed vessel in the absence of air by an incandescent tube or wire or by an electric spark. Frank[116] decomposed a mixture of acetylene and carbon monoxide or dioxide to produce a carbon free from tarry condensation products.

In the process used by Machtolf,[117] acetylene under pressures of up to about 6 atmospheres was exploded by an electric spark to produce hydrogen and lampblack. Mixtures of hydrocarbons with oxides of carbon or other gases, which cannot be exploded at ordinary temperature and under pressure, have been found by Gollmert[118] to explode if heated and to yield finely divided carbon. Combustion of a mixture consisting of acetylene, an indifferent gas and a metal carbonyl can be provoked by a single short charge of energy, a method proposed for the production of carbon.[119] Other methods of exploding or otherwise decomposing acetylene by heat have been suggested by Morehead,[120] Pictet,[121] Wegelin,[122] and Bosch.[123] Pictet[124] proposed to decompose hydrocarbons containing acetylene in a tube, the first portion of which was heated to about 500° C. At this temperature acetylene decomposes into its elements with a considerable evolution of heat, which renders the continuous decomposition independent of external heat. In like manner Waterman and Tulleners[124a] decompose ethylene

[112] *Acetylen in Wiss. u. Ind.*, 1930, **33**, 97; *Chem. Abs.*, 1930, **24**, 6019.

[113] Dépierre, *Bull. soc. ind. Mulhouse*, 1901, 189; *J.S.C.I.*, 1901, **20**, 890.

[114] *U. S. Bur. Mines Bull.* **192**, 1922.

[114a] A comparison of the properties of acetylene blacks is given by Haufman, *Chemical Markets*, 1933, **33** (3), 217.

[115] German Patent 103,862, 1898; *Chem. Zentr.*, 1899, **2**, 896. British Patent 7,139, 1898; *J.S.C.I.*, 1899, **18**, 284; U. S. Patent 671,672, April 9, 1901; *Eng. and Mining J.*, 1898, July 9, 35; *J.S.C.I.*, 1898, **17**, 711. *Cf.* Dépierre, *Bull. soc. ind. Mulhouse*, 1901, 189; *J.S.C.I.*, 1901, **20**, 890.

[116] German Patent 112,416, 1899; *Chem. Zentr.*, 1901, **2**, 827; British Patent 12,211, 1899; *J.S.C.I.*, 1900, **19**, 545; *Z. angew. Chem.*, 1905, **18**, 1733; *Chem. Ztg.*, 1905, **29**, 1044; *J.S.C.I.*, 1905, **24**, 1117.

[117] French Patent 364,034, 1906; *Chem. Abs.*, 1907, **1**, 2326; British Patent 14,601, 1906; *Chem. Abs.*, 1907, **1**, 2514. U. S. Patents 872,949 and 872,950, Dec. 3, 1907; *Chem. Abs.*, 1908, **2**, 1199, German Patents 194,301 and 194,939, 1905; *Chem. Abs.*, 1908, **2**, 2023; British Patent 13,865, 1909. *Chem. Abs.*, 1911, **5**, 1676. See also Machtolf, Bosch, Closs, G. and T. Boehn, German Patent 207,520, 1907; *Chem. Abs.*, 1909, **3**, 1964; German Patent 212,345, 1908; *Chem. Abs.*, 1909, **3**, 2864. Acetylene black was manufactured by a process of this character at the plant of the Carbonium Co., which was destroyed by explosion during the summer of 1910; see *Chem. Met. Eng.*, 1911, **9**, 157.

[118] German Patent 212,202, 1907; *J.S.C.I.*, 1909, **28**, 1050.

[119] I. G. Farbenindustrie A.-G., French Patent 720,192, 1931; *Chem. Abs.*, 1932, **26**, 3884. British Patent 364,757, 1930; *Brit. Chem. Abs.* **B**, 1932, 298.

[120] U. S. Patent 779,728, Jan. 10, 1905; assigned to Union Carbide Co.; *J.S.C.I.*, 1905, **24**, 142; U. S. Patent 986,489, Mar. 14, 1911; assigned to Union Carbide Co.; *Chem. Abs.*, 1911, **5**, 1991.

[121] British Patent 24,256, 1910; *Chem. Abs.*, 1912, **6**, 145.

[122] German Patent 198,646, 1907; *Chem. Abs.*, 1908, **2**, 2631. German Patent 201,262, 1907; *Chem. Abs.*, 1909, **13**, 115.

[123] German Patent 270,199, 1913; *J.S.C.I.*, 1914, **33**, 429; *cf.* German Patent 268,291, 1911; *Chem. Abs.*, 1914, **8**, 1663.

[124] British Patent 24,256, 1910; *Chem. Abs.*, 1912, **6**, 145. German Patent 255,733, 1909; *Chem. Abs.*, 1913, **7**, 1967. French Patent 421,838, 1910; *Chem. Abs.*, 1912, **6**, 1968.

[124a] *J. Inst. Pet. Tech.*, 1931, **17**, 506; *Brit. Chem. Abs.* **A**, 1931, 1147.

explosively, by heating in an autoclave at 350° C. under a pressure of about 170 atmospheres.

Apparatus for the explosive decomposition of acetylene has been described by Machtolf[125] and by the Hydrocarbon A.-G. für Chemische Produkte.[126] Rimarski and his co-workers[127] reported that detonation must be avoided in the commercial manufacture of acetylene black. This is done by holding pressures at or below a definite low starting pressure or by diluting acetylene with a gas such as hydrogen or oil gas.

DECOMPOSITION EFFECTED IN THE PRESENCE OF CATALYSTS

With catalysts the thermal decomposition of hydrocarbons to carbon and hydrogen can be effected at somewhat lower temperatures than those ordinarily required. Cantelo[128] studied the thermal decomposition of methane in the presence of silica gel, manganese dioxide, calcium oxide, bone black, and mixtures of copper and copper oxide, nickel and nickel oxide, and iron and ferric oxide, and suggested the use of such catalysts to lower reaction temperatures to improve the quality of the black produced. As pointed out previously, the activity of catalysts is impaired when carbon is deposited on their surfaces, and therefore some provision must be made for its removal or for preventing its deposition.

An investigation of the decomposition of a kerosene fraction, boiling from 200° to 230° C., by passing its vapors over heated pumice impregnated with metallic cobalt, iron, nickel and manganese was made by Kanning and Brown.[129] They noted that the catalyst was poisoned by carbon deposited at low temperatures, although no such effect was observed at high temperatures. The ability of these catalysts to decompose kerosene vapors decreases in the order given. Cobalt was effective as a catalyst for continuous conversion at temperatures above 500° C. Increasing the temperature increased the proportion of hydrogen in the gaseous products and decreased the proportion of methane. Although in all cases increasing the temperature increased the decomposition of the kerosene vapors, at higher temperatures an increase was noted in the percentage of hydrogen in the gaseous products in the presence of cobalt and nickel. Under similar conditions with iron and manganese catalysts the percentage of methane was increased. When a nickel catalyst was used a relatively large percentage of unsaturated hydrocarbons was formed in contrast to only traces with cobalt. With both nickel and manganese large quantities of paraffin hydrocarbons other than methane were also formed. In the presence of iron at 400° C. the gas contained the largest percentage of hydrogen (90.5 per cent) and with nickel at 390° C. it had the greatest percentage of methane (46.4 per cent).

In the decomposition of hydrocarbons at temperatures below 1000° C., the formation of soot may be avoided by using two catalysts of different powers.[129a] The gas is led over the less active catalyst first, and hydrogen and higher hydrocarbons are produced.

Good yields of carbon black were obtained by Bancroft[130] by decomposing methane at 1200° C. or higher. In his process the hydrocarbon gas is passed between the concave bottom of a flame-heated combustion chamber and a rotating steam- or water-cooled drum, the surface of which is parallel with the hot surface of the combustion chamber. The heating surface may be composed of copper, nickel, or other materials exerting a catalytic effect. The carbon formed is subjected to a high temperature for only a short time, being quickly removed from the cracking zone and scraped from the rotating drum.

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[125] U. S. Patent 1,746,003, Feb. 4, 1930; assigned to C. Hostmann-Steinberg'sche Farbenfabrik, G.m.b.H.; *Brit. Chem. Abs.* **B**, 1930, 805; British Patent 340,235, 1929; *Brit. Chem. Abs.* **B**, 1932, 286. U. S. Patent 1,782,540, Nov. 25, 1930; assigned to C. Hostmann-Steinberg'sche Farbenfabr. G.m.b.H.; *Brit. Chem. Abs.* **B**, 1931, 664; British Patent 341,235, 1929; *Chem. Abs.*, 1931, **25**, 4095.

[126] British Patent 264,500, 1927; assigned to Burger; *Brit. Chem. Abs.* **B**, 1928, 560.

[127] Rimarski, Pleus, Friedrich, Streb, Noack, Kemper, Hoffmann and Konschak, *Jahresber. Chem.-tech. Reichanstalt,* 1930, **8**, 47; *Chem. Zentr.*, 1931, 1, 2417; *Chem. Abs.*, 1932, **26**, 4419.

[128] *J. Phys. Chem.*, 1924, **28**, 1036. See Chapter 2.

[129] *J. Phys. Chem.*, 1931, **35**, 2689; *Chem. Abs.*, 1931, **25**, 5829.

[129a] I. G. Farbenindustrie A.-G., French Patent 729,429, 1932; *Chem. Abs.*, 1932, **26**, 6079.

[130] U. S. Patent 1,390,480, Sept. 13, 1921; *Chem. Abs.*, 1922, **16**, 320.

Crommett, Hawkins and Wheelock[131] passed methane or other hydrocarbon gases through a tube lined with palladium, nickel, manganese, or a similar metallic catalyst and heated externally to about 700° C. The carbon black formed in good yield is pushed out of the tube at regular intervals by a ram. The temperature of the catalyst should be varied somewhat (for example, between a temperature of 700° and 750° C. with palladium) by providing a secondary varying source of heat.

For the decomposition of unsaturated hydrocarbons (ethylene, acetylene and diacetylene) to produce carbon black the use of a metal of the iron group (nickel or cobalt) or its oxide has been suggested as a dehydrogenating catalyst by Schmidt and Grosskinsky.[132] The hydrocarbons are treated at a temperature of 300° to 450° C. under a pressure of 30 to 100 atmospheres. The reaction may be effected similarly under reduced pressure[133] and in the presence of other gases such as hydrogen, water vapor, oxides of carbon, and methane. Activators (alkali or alkaline-earth metals or oxides of zinc, cadmium, copper, chromium, vanadium, molybdenum, uranium, or alkalies) may be used with the catalyst.[134] The deposition of iron or nickel catalysts on supports such as charcoal or magnesium oxide for use in the catalytic decomposition of methane into carbon and hydrogen was suggested by Grünstein.[135]

Haag, Schlecht and Schubardt[136] employed a metal carbonyl in effecting the dehydrogenation of olefins and diolefins to carbon black. A catalyst composed of nickel or iron (prepared by decomposing a carbonyl compound) and an alkali metal compound, such as potassium carbonate, was proposed by Haag.[137] Other suggested catalysts include a mixture of at least two solid oxides which are not reduced to metals in the process.[138] Such mixtures may be made from the oxides of aluminum, boron, zirconium, silicon, cerium, thorium, and the alkaline earths. The decomposition can also be effected in the presence of mixtures of metallic oxides of the iron group with acid-forming oxides of metals of groups IV, V, or VI of the periodic system or the compounds formed between oxides of metals of these two types (nickel vanadate) may be substituted.[139]

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[131] U. S. Patent 1,528,099, March 3, 1925; assigned to Hawkins and Wheelock; *Chem. Abs.*, 1925, **19**, 1477; also U. S. Patent 1,772,984, Aug. 12, 1930; *Chem. Abs.*, 1930, **24**, 5118.

[132] U. S. Patent 1,868,919, July 26, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.* 1932, **26**, 5391. I. G. Farbenindustrie A.-G.; British Patent 324,959, 1928; *Chem. Abs.*, 1930, **24**, 3866; British Patent 327,548, 1929; *Chem. Abs.*, 1930, **24**, 5117; British Patent 346,680, 1929; *Chem. Abs.*, 1932, **26**, 568; French Patent 700,252, 1930; *Chem. Abs.*, 1931, **25**, 3781. German Patent 565,556, 1928; *Chem. Abs.*, 1933, **27**, 2540; addn. to German Patent 552,623; *Chem. Abs.*, 1932, **26**, 5711. See also Grosskinsky and Treppenhauer, U. S. Patent 1,894,764, Jan. 17, 1933, assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2540.

[133] Schmidt and Grosskinsky, U. S. Patent 1,868,920, July 26, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 5391; I. G. Farbenindustrie A.-G.; British Patent 327,374, 1928; *Brit. Chem. Abs.* **B**, 1930, 545.

[134] Schmidt and Grosskinsky, U. S. Patent 1,868,921, July 26, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 5391; I. G. Farbenindustrie A.-G., British Patent 325,207, 1928; *Chem. Abs.*, 1930, **24**, 4127; British Patent 353,622, 1930; *Chem. Age* (*London*), 1931, **25**, 452. Grosskinsky, U. S. Patent 1,906,462, May 2, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3567.

[135] French Patent 704,601, 1930; *Chem. Abs.*, 1931, **25**, 4671. The use of carbon black containing more than 2 to 3% iron is described by Grünstein in French Patent 730,944, 1932; *Chem. Abs.*, 1933, **27**, 381. See also British Patent 363,735, 1930; *Chem. Abs.*, 1933, **27**, 1722; British Patent 380,893, 1932; *Chem. Abs.*, 1933, **27**, 4039.

[136] German Patent 549,348, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3884.

[137] U. S. Patent 1,882,813, Oct. 18, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 817.

[138] I. G. Farbenindustrie A.-G., British Patent 359,620, 1930; *Chem. Abs.*, 1932, **26**, 4922; French Patent 710,626, 1931; *Chem. Abs.*, 1932, **26**, 1728; Hennicke, German Patent 565,387, 1930, assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 1110.

Since the efficiency of catalysts decreases as they become coated with carbon, they may be allowed to fall through the heated gas stream.[140] The deposition of carbon on any particular particle is thus minimized and fresh catalyst is always present. The catalysts may be readily separated from the carbon, for example, by flotation, magnetic separation or solution in an acid. To overcome this decreasing efficiency it has been proposed to use the catalysts in the form of balls or cylinders which roll freely in a rotating furnace and which by this continuous motion remove the sooty deposit from the active surface.[141] Decomposition may also be conducted in a non-sparking electric field in the presence of these catalysts.[142]

In the catalytic decomposition of hydrocarbons lining the reaction chamber with materials which produce no appreciable decomposition (silver, copper, chromium, or their alloys, or ferrosilicon) has been proposed to prevent clogging of the apparatus.[143]

Decomposition Effected with Chlorine and Chlorine Compounds

A number of methods of making carbon in which a hydrocarbon is treated with chlorine or a chlorine compound have been advanced.[143a] Thus, Averill[144] burned natural gas in an atmosphere of chlorine, forming hydrogen chloride and lampblack. Mott[145] heated chlorine and methane to yield carbon tetrachloride, which was subsequently heated with more methane to produce lampblack and hydrochloric acid.

Winter[146] burned a mixture of hydrocarbon (vapor or gas) and chlorine in an atmosphere of air to obtain high yields of a very pure carbon and hydrogen chloride. Such a flame consists of a highly luminous interior zone where the chlorine reacts with the hydrocarbons, and an outer oxidation mantle. Gaseous products are separated from the carbon by filtration or electrical precipitation and are washed with water to remove the hydrogen chloride.

The use of chlorine or of hydrogen chloride in the production of carbon black has also been described by Baxter. In one process the hydrocarbons are cracked in the vapor phase in the presence of hydrogen chloride and the resulting products are further treated with chlorine to yield carbon and hydrogen chloride.[147] A chlorinated hydrocarbon can be mixed with untreated hydrocarbon (as for example, carbon tetrachloride with methane) and the mixture subsequently burned.[148] Best results are obtained from such mixtures in which the total chlorine does not exceed the equivalent of hydrogen. The carbon black obtained by such processes can be freed of volatile matter by dispersing it in a gas, such as nitrogen, carbon dioxide or steam, at temperatures of 150° to 900° C.[149] The hydrogen chloride formed can be used again either as such or as a source of chlorine.[150]

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[139] Bataafsche Petroleum Maatschappij, French Patent 731,652, 1932; *Chem. Abs.*, 1933, 27, 816; British Patent 381,072, 1932; *Brit. Chem. Abs.* **B**, 1932, 1119.

[140] I. G. Farbenindustrie A.-G., British Patent 357,135, 1930; *Brit. Chem. Abs.* **B**, 1931, 1083; British Patent 361,837, 1930; *Brit. Chem. Abs.* **B**, 1932, 170.

[141] I. G. Farbenindustrie A.-G., British Patent 340,239, 1929; *Chem. Abs.*, 1931, 25, 4096.

[142] Schmidt and Grosskinsky, U. S. Patent 1,813,514, July 7, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 5257. I. G. Farbenindustrie A.-G., British Patent 326,913, 1929; *Brit. Chem. Abs.* **B**, 1930, 545.

[143] I. G. Farbenindustrie A.-G., British Patent 358,178, 1930; *Chem. Abs.*, 1932, 26, 4924.

[143a] Nash and Mason (*Ind. Eng. Chem.*, 1934, 26, 45) reviewed the action of halogens in the heat treatment of hydrocarbons.

[144] U. S. Patent 1,238,734, Sept. 4, 1917; *Chem. Abs.*, 1917, 11, 3393.

[145] U. S. Patent 1,259,121, Mar. 12, 1918; assigned to National Carbon Co.; *Chem. Abs.*, 1918, 12, 1413.

[146] British Patent 317,165, 1928; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.* 1929, 24, 1941; Imperial Chemical Industries, Ltd., German Patent 552,466, 1929; *Chem. Abs.*, 1932, 26, 4425.

[147] British Patent 346,858, 1930; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1730.

In another process,[151] in which hydrogen, acetylene, ethylene and carbon black are the products, methane is treated at temperatures of 950° to 2000° C., at pressures varying from 760 mm. to 25 mm., for periods varying from about 15 seconds to 0.01 second, the required pressure and time of heating required decreasing with rising temperature. The gases formed are continuously withdrawn by suction, a halogen or halogen compound is used as a catalyst, and the ratio of the surface to the volume of the apparatus varies from about 3:1 at 950° to 30:1 at 2000° C. in this method.

PETROLEUM COKE

Petroleum coke is a hard, porous, glistening material, varying in color from slate-gray to black, left as the solid residue from the destructive distillation of petroleum hydrocarbons. In appearance it is similar to the so-called by-product coke made from coal. There are two types of petroleum coke, namely, that produced in coking stills and that formed in cracking operations. The first has been a product of the refining industry for more than a half-century, while the latter has become the principal petroleum coke since the adoption of cracking processes (generally introduced about 1915). Although the quantity of coke formed in coking-still operations has remained fairly constant for many years, the production of cracking-still coke has increased from approximately 200,000 tons in 1921 to nearly 1,100,000 tons in 1928.[152]

In coking stills, crude oils are distilled (usually at atmospheric pressure) until all but about 8 per cent of the volatile constituents of the residue have been driven off. This leaves a layer of coke at the bottom, which may range from 6 inches thick from a Mid-Continent crude to 30 inches from a Mexican crude. The distillation is a batch operation and the still is allowed to cool between runs so that the coke can be broken up and removed.

Cracking stills are usually operated continuously, often under increased pressure. The greater part of the coke formed is deposited in the reaction chamber where a substantial part of the conversion occurs, and its quantity depends upon the character of the charging stock, the temperature, the duration of heating and the pressure.

From a chemical point of view, petroleum coke is to be regarded not as an elementary form of carbon but as a mixture of hydrocarbons containing high percentages of carbon and small percentages of hydrogen.[153] Many hydrocarbons of high melting point comprising the final distillation products of petroleum have been isolated and studied.[154] These are probably intermediates in the pyrolytic decomposition of hydrocarbons to form petroleum coke.[155] Morton[156] obtained from petroleum residues a yellow-green material, crystallizing in needles with a pearly luster. This material, which appeared to be isomeric with anthracene, was called *viridine* and later *thallene*.[157] A compound called *petrocene* was obtained by Tweddle by the redistillation of petroleum residues.[158] It was a green crystalline body having a specific gravity of 1.206 and from it, by distillation, were separated various fractions which were called *carbocene, carbopetrocene,* and *thallene*. Hemilian[159] isolated a hydrocarbon from the highest boiling portions of American petroleum. This compound crystallized from benzene in shining yellow plates melting above 300° C. and was also called petrocene. From Morton's thallene, Smith[160] isolated picene, which had previously been described and obtained in the distillation of brown coal by Burg.[161] Graebe and Walter[162] also isolated picene (see Chapter 2), melting at 330° to 335° C., from the residues of the distillation of Californian petroleum.

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[148] British Patent 343,477, 1929; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, 25, 4369.

[149] British Patent 343,108, 1929; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, 25, 4368.

[150] British Patent 343,676, 1930; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, 25, 4368.

[151] International Industrial and Chemical Co., Ltd., British Patent 352,688, 1929; assigned to Soc. industrielle des hydrocarbures et dérivés; *Chem. Abs.*, 1932, 26, 3341.

[152] Swanson, *U. S. Bur. Mines Economic Paper* 9, 1930.

[153] Morrell and Egloff, *J.S.C.I.*, 1932, 51, 467. See also Gurwitsch and Moore, "The Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, 1932, 335.

[154] A comprehensive review of this field is given by Zaloziecki and Gans, *Chem.-Ztg.*, 1900, 24, 535, 553.

Prunier and David[163] separated a green crystalline body by the redistillation of petroleum residues. This appeared to be a mixture of the fluorescent coloring matter of American petroleum with aromatic hydrocarbons of higher molecular weight than those known at the time. The carbon content of this material varied from 88 to 96 per cent. On treating it with various solvents, Prunier[164] succeeded in isolating a granular crystalline substance soluble in carbon disulphide and in hot chloroform. On evaporating a solution in the latter solvent, a reddish-brown residue, corresponding to the formula $(C_6H_2)_n$, remained. From this residue, other bodies evidently belonging to a new series of hydrocarbons and having equally high carbon contents were isolated. Thus, from its solution in a mixture of alcohol and a little chloroform there were crystallized yellowish slender needles with a pearly luster, melting at 260° C., nearly insoluble in alcohol, ether and warm chloroform, but soluble in petroleum, benzene, and acetic acid. This compound, also corresponding to the formula $(C_6H_2)_n$, formed two picrates having the formulas $C_{24}H_8C_6H_3(NO_2)_3O$ and $C_{24}H_8{\cdot}2C_6H_3(NO_2)_3O$, melting at 185° and 135° C., respectively.

Prunier and Varenne[165] also examined the dark, spongy, brittle residue left in the retorts from the distillation of petroleum, the so-called petroleum coke. A portion of this residue was soluble in carbon disulphide and this extract (containing 93 to 95 per cent carbon) was separated into fractions by means of various solvents. The alcohol-soluble fraction was a pale yellow viscous, oxygenated substance, the ether-soluble fraction was a mixture of orange-colored crystalline hydrocarbons and oxygenated compounds, and the acetic acid-soluble fraction was dark brown and appeared to be the substance to which the fluorescence of petroleum was due. The insoluble portion contained 97.4 to 98.0 per cent carbon.

Sadtler and McCarter[166] separated several hydrocarbons occurring in petrocene. One, melting at 280° C., had the composition of a dimethylanthracene,

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[155] Brooks (*Ind. Eng. Chem.*, 1926, 18, 518) believes coke results through the intermediate formation of complex benzenoid hydrocarbons.

[156] *J. Franklin Institute*, 1872, 64, 1872.

[157] *Chem. News*, 1876, 34, 188.

[158] Zaloziecki and Gans, *loc. cit.*; also *Chem. Soc. Abs.*, 1879, 36, 309.

[159] *Ber.*, 1877, 9, 1604; *Chem. Soc. Abs.*, 1877, 32, 867; *Chem. Zentr.*, 1877, 2.

[160] *Monit. scient.*, 1880, 22, 68.

[161] *Ber.*, 1876, 9, 1207; *Chem. Soc. Abs.*, 1877, 31, 96; *Ber.*, 1880, 13, 1834; *Chem. Soc. Abs.*, 1881, 40, 179.

[162] *Ber.*, 1881, 14, 175; *Chem. Soc. Abs.*, 1881, 40, 284.

[163] *Compt. rend.*, 1878, 86, 991; *Chem. Soc. Abs.*, 1879, 36, 309; *Ber.*, 1879, 12, 366.

[164] *Compt. rend.*, 1879, 88, 316; *Chem. Soc. Abs.*, 1879, 36, 447; *Ber.*, 1879, 12, 843.

[165] *Bull. soc. chim.*, 33, 567; *Compt. rend.*, 1880, 90, 1006; *Chem. Soc. Abs.*, 1881, 40, 239; *Chem. Zentr.*, 1880, 359, 548; *Ber.*, 1880, 13, 1141.

[166] *Amer. Chem. J.*, 1879, 1, 30; *Chem. Soc. Abs.*, 1881, 40, 1128.

$C_{16}H_{14}$, although its properties did not agree with those of any of the then known isomers. The hydrocarbon melting at 178° appeared to be a monomethylanthracene. Both of these substances were undoubtedly contaminated with chrysene, a compound having a higher percentage of carbon and which was extremely difficult to remove. Divers and Nakamura[167] isolated a yellow and a colorless hydrocarbon, both corresponding to the formula $(C_4H_3)_n$ and melting at 280°-285° C., from the last portions of the distillation of a Japanese petroleum. From a Russian mazout, de Boissieu[168] similarly obtained a substance melting at 145°-150° C. The isolation of a hydrocarbon, $C_{24}H_{18}$, called *crackene*, from the pitch of a Saxon lignite tar has been reported by Klaudy and Fink.[169] This compound was believed to be identical with the hydrocarbon $(C_4H_3)_n$ obtained by Divers and Nakamura and with benzerythrene, formed in passing benzene vapor through a red-hot tube.[170]

Zaloziecki and Gans[171] isolated a series of hydrocarbons corresponding to the general formula C_nH_{2n-20} from crude petrocene and to this series they have given the name petrocenes. The melting points of the various hydrocarbons were 140°, 147°, 153°, 155.5°, 168°, 191.5°, 205°, 216°, 221.5°, 228°, 245°-247° and 250.5° C. The compound melting at 250.5° C. had the composition $C_{15}H_{10}$, and yielded a picrate melting at 178° and a bromo-derivative melting at 276° C. When treated with various oxidizing agents no well-defined products were formed but with fuming nitric acid, yellow nitro-derivatives were obtained.

According to Zerbe and Eckert,[171a] the destructive distillation of pitch yields naphthalene, acenaphthene, fluorene, phenanthrene, carbazole, anthracene, methylanthracene, acridine, fluoranthene, naphthofluorene, pyrene, chrysene, and phenylnaphthylcarbazole.

Proximate analyses of cracking- and coking-still cokes, reported by Morrell and Egloff,[172] are given in Table 48:

TABLE 48.—*Proximate Analyses of Cracking- and Coking-Still Cokes.*

Coke Source from Fuel Oils	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulphur	B.T.U. per lb.
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	
Cracking stills						
Mid-Continent	0.50	8.07	91.81	0.05	0.83	15,645
Panhandle, Texas	3.31	14.00	81.12	1.59	0.45	15,573
Arkansas	0.11	12.28	87.15	0.46	4.18	15,898
Kentucky	0.39	11.65	87.42	0.54	0.66	16,403
Pennsylvania	0.20	11.39	87.42	0.99	0.22	16,248
California	0.47	18.03	80.49	0.91	1.09	15,295
Coking stills						
	0.6	2.1	95.8	1.5	0.5	14,480
	0.3	3.9	94.1	1.0	0.7	14,900

Petroleum coke had been a valueless by-product during early years of petroleum refining but has lately been utilized in many diverse ways. The greater part is being used as a fuel,[173] for which purpose it possesses many advantages over powdered coal. Petroleum coke ignites at a lower temperature, the flame propagates faster, the ash content is lower, and it is more easily pulverized.[174] For domestic use, briquettes of petroleum coke are said to be an excellent fuel.[175] Building blocks are made from petroleum coke by mixing the coke with about one-third as much of a binder formed from Portland cement and petroleum coke fines.[175a] Other uses include the manufacture of carbon electrodes,[176] carbon brushes, crucibles, dry cells, and in the form of bricks for electrolytic cells and furnace linings. As it is a reducing agent it has found use in some metallurgical processes and in the reduction of barite to barium sulphide for the manufacture of lithopone. According to Swanson,[177] it is also finding application in the ceramic, cement and abrasives industries as a fuel. Swanson also states that California fruit growers use it for their orchard fires and according to Morrell and Egloff [178] it is now being used for curing "hickory smoked hams."

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[167] *J.C.S.*, 1885, **47**, 924.

[168] *Chem.-Ztg.*, 1893, **17**, 70.

[169] *Monatshefte,* 1900, **21**, 118; *Chem. Soc. Abs.*, 1900, **78** (1), 284; *Chem.-Ztg.*, 1900, **24**, 60.

[170] Schultz, *Ber.*, 1878, **11**, 95; *Chem. Soc. Abs.*, 1878, **34**, 323; Schmidt and Schultz, *Ann.*, 1880, **203**, 118; *Chem. Soc. Abs.*, 1881, **40**, 435.

[171] *Chem.-Ztg.*, 1900, **24**, 553; *Chem. Soc. Abs.*, 1900, **78** (1), 593.

[171a] *Brennstoff-Chem.*, 1933, **14**, 1; *Brit. Chem. Abs.* **B**, 1933, 210.

[172] *J.S.C.I.*, 1932, **51**, 467. Analyses have previously been given by Lidov, *J. Russ. Phys.-Chem. Soc.*, 1882, **14**, 323; *Chem. Soc. Abs.*, 1883, **44**, 408. Doeltz, *Chem.-Ztg.*, 1906, **30**, 585; and Langbein, *Chem.-Ztg.*, 1906, **30**, 1115; and analyses of ash by Shirey, *Ind. Eng. Chem.*, 1931, **23**, 1151.

A number of methods for the production of petroleum coke have been described. Nomi [179] distilled petroleum tar destructively at 500° to 600° C. To obtain coke in the form of irregular scales, Perry [180] heated a thin layer of coal tar, pitch, petroleum, or asphalt on a hot drum. Murray and Ricketts [181] produced coke from oil residues by bringing hot gases into contact with them as they flow in a thin film over the inner surface of a coking chamber. Distillation of heavy hydrocarbon liquids to hard low-volatile cokes was accomplished by Jennison and Faben [182] by passing gases produced by the combustion of carbonaceous fuel into the liquids. Campbell and Herthel [183] and Gullette [184] reduced heavy oils to coke in cylindrical vessels, removing the coke subsequently *en bloc*. An apparatus for the production of petroleum coke was described by Steinschneider,[185] and Tz [186] proposed a method of operating cracking units to produce ash-free petroleum coke. Also, heavy oils may be sprayed into an oven chamber heated from below by horizontal flues. Part of the hot combustion gases from the flues mixed with air is passed in with the oils to attain the temperature necessary for cracking.[186a]

Petroleum coke formed in the cracking of oils can be removed from the residues by filtration. Egloff and Benner [187] obtained purified carbon by washing the residue from the filtration with solvents. The removal of finely divided solid material from distillation gases by washing with water heated to such a temperature that the hydrocarbons ordinarily solid are separated from the gases in the liquid state has also been described.[188]

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[173] Egloff, *Oil and Gas J.*, *Oct.* 4, 1923, **22**, 188, 194, 196. Morrell and Egloff, *J.S.C.I.*, 1932, **51**, 467; Wallace, *Oil and Gas J.*, 1930, **29**, No. 20, 91, 360. Dunstan, *Refiner*, 1930, **9**, No. 7, 125; No. 8, 120; *Chem. Abs.*, 1930, **24**, 5987.

[174] Schulz, *Refiner and Natural Gas Mfr.*, 1930, **9**, No. 1, 55; *Chem. Abs.*, 1930, **24**, 1963.

[175] Morrell and Egloff, *loc. cit.* See also Fischer, *Natl. Petroleum News*, 1931, **23** (24), 46, 52; *Chem. Abs.*, 1931, **25**, 4391.

[175a] Cramer, U. S. Patent 1,915,051, June 20, 1933; *Chem. Abs.*, 1933, **27**, 4371.

[176] Clacher, *Chem. Met. Eng.*, 1911, **9**, 137; *Chem. Abs.*, 1911, **5**, 1714. Yardley, *Chem. Met. Eng.*, 1922, **26**, 321; *Chem. Abs.*, 1922, **16**, 1707. Mantell, *Chem. Met. Eng.*, 1922, **27**, 109, 161; *Chem. Abs.*, 1922, **16**, 3263, 3444. The use of petroleum carbon electrodes for the aluminum industry is described by Lewis, *The Atlantic Connecting Rod*, Sept. 1922, 19 (published by Atlantic Refining Co., Philadelphia, Pa.).

[177] Swanson, *U. S. Bur. Mines Economic Paper* **9**, 1930.

[178] *Loc. cit.*

[179] Japanese Patent 31,647, 1917; *Chem. Abs.*, 1918, **12**, 1250; U. S. Patent 1,386,945, Aug. 9, 1921; *Chem. Abs.*, 1921, **15**, 3905.

[180] U. S. Patent 1,257,959, Feb. 26, 1918; *Chem. Abs.*, 1918, **12**, 993.

[181] U. S. Patent 1,293,866, Feb. 11, 1919; *Chem. Abs.*, 1919, **13**, 1147.

[182] U. S. Patent 1,749,138, March 4, 1930; assigned to Jennison; *Chem. Abs.*, 1930, **24**, 2278.

[183] U. S. Patent 1,872,884, Aug. 23, 1932; assigned to Sinclair Refining Co.; *Chem. Abs.*, 1932, **26**, 6117.

[184] U. S. Patent 1,872,938, Aug. 23, 1932; assigned to Sinclair Refining Co.; *Chem. Abs.*, 1932, **26**, 6118.

[185] *Petroleum Z.*, 1921, **17**, 473; *Chem. Abs.*, 1922, **16**, 1660.

[186] *Azer. Neft. Khoz.*, 1932, No. 3, 89; *Chem. Abs.*, 1932, **26**, 5747.

[186a] British Patent 385,610, 1931; assigned to Brassert-Tidewater Development Corp.; *Brit. Chem. Abs.* **B**, 1933, 259.

[187] U. S. Patent 1,535,211, April 28, 1925; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1925, **19**, 1944.

A method of calcining petroleum coke in a rotary kiln was proposed by Walden.[189] In his method of making carbon black, Oberle[190] treated finely disintegrated petroleum carbon with superheated steam. An activated carbon can also be produced[191] by heating petroleum coke in the presence of water and lime to a temperature of 480° to 510° C. or by mixing petroleum coke with sawdust and acid sludge followed by treatment with highly superheated steam.

Steinkopf and Winternitz[192] determined the asphalt content of various oils and the amounts of coke formed from them, both *in vacuo* and at atmospheric pressure. They found that 40 per cent of the hard asphalt present and from 40 to 60 per cent of the soft asphalt were converted into coke. Distillations under reduced pressure yielded less coke than distillations at atmospheric pressure. The best yields of coke from petroleum tars distilled in gas-oven retorts are obtained, according to Allner,[193] at a temperature of 1100° C.

The graphitization of petroleum coke at 2500° C. and the relative catalytic effect of various metals on this process have been studied by Schleifstein.[194] Calcium was found to have the least effect, and boron and chromium had the greatest. All attempts to graphitize petroleum coke in the presence of small proportions of silica, even by heating for 15 hours at 2400° to 2500° C., were complete failures.

PURIFICATION OF HYDROGEN

When hydrogen is generated by the purely thermal decomposition of hydrocarbons, the only impurities usually present in the product are small amounts of hydrocarbons (principally methane) and perhaps some nitrogen. It is extraordinarily difficult to effect complete decomposition of hydrocarbons even at high temperatures, since equilibrium in such pyrolytic processes is approached so slowly. By the pyrolysis of a Polish natural gas at 1700° C., Mantel[195] obtained hydrogen which still contained 0.7 per cent of methane. In many of the processes already outlined, the resulting hydrogen is contaminated by oxides of carbon and small amounts of gaseous hydrocarbons. These impurities are present also in gases produced by the reaction of hydrocarbons with steam at high temperatures (see Chapter 10). The present discussion must necessarily be limited to a brief account of the methods for the removal of only these impurities.

The purity of the hydrogen required for various purposes varies greatly. For certain hydrogenation processes (e.g., coal hydrogenation) a comparatively impure gas is probably quite satisfactory. On the other hand, the hydrogen employed in the catalytic synthesis of ammonia must be free from traces of oxygen, carbon monoxide and water vapor.[196]

Kloepfer[196a] treated the gases (containing hydrogen and methane) with a mixture of 25 to 35 per cent of fused sodium and 70 to 75 per cent of a diluent such as sodium chloride or carbonate. The mixture was heated to a temperature of over 300° C. in order to melt the sodium, but at a low enough temperature to keep the diluent solid.

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[188] Heinrich Koppers A.-G.; German Patent 536,209, 1929; *Chem. Abs.*, 1932, **26**, 1113.

[189] U. S. Patent 1,564,730, Dec. 8, 1925; *Chem. Abs.*, 1926, **20**, 495.

[190] U. S. Patent 1,763,063, June 10, 1930; *Chem. Abs.*, 1930, **24**, 3866.

[191] Oberle, U. S. Patents 1,763,101 and 1,763,102, June 10, 1930; *Brit. Chem. Abs.* **B**, 1931, 9.

[192] *J. pr. Chem.*, 1920, **101**, 82; *Chem. Abs.*, 1921, **15**, 943.

[193] *Petroleum Z.*, 1922, **18**, 1337, 1369; *Chem. Abs.*, 1923, **17**, 2185.

[194] *Can. Chem. Met.*, 1928, **12**, 59; *Chem. Abs.*, 1928, **22**, 1732.

[195] *Przemysl Chem.*, 1928, **12**, 333; *Chem. Abs.*, 1928, **22**, 4458.

[196] Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, **1930**, 858; Taylor, "Industrial Hydrogen," Chemical Catalog Co., Inc., New York, **1921**, 171.

[196a] U. S. Patent 1,855,355, Apr. 26, 1932; assigned to Deutsche Gold- und Silber-Scheideanstalt. vorm. Roessler; *Brit. Chem. Abs.* **B**, 1933, 267.

PURIFICATION BY FRACTIONAL CONDENSATION

One method for obtaining substantially pure hydrogen from mixtures is low-temperature fractionation. This process was developed principally for producing hydrogen from water gas[197] (a mixture of hydrogen and carbon monoxide chiefly) but it has been modified to produce hydrogen from coal gas or coke-oven gas. One method for separating the constituents of coke-oven gas by fractional condensation has been described by Bronn.[198] The gas, previously freed from carbon dioxide by washing successively with water under a pressure of 12 atmospheres and with caustic soda, is subjected to a preliminary cooling to —30° C. to —50° C. by heat interchange with the gases issuing from the system. The gas then enters a separation chamber where it undergoes further cooling by the gases already separated. All the constituents are thus condensed with the exception of hydrogen, nitrogen, and part of the carbon monoxide. The residual gas, still under a pressure of about 10 atmospheres, is then passed through tubes immersed in a bath of liquid nitrogen evaporating under reduced pressure. This effects condensation of the carbon monoxide and almost all the nitrogen, leaving hydrogen of about 98 to 99 per cent purity. If the gases are to be used for the synthesis of ammonia, the residual mixture of hydrogen, nitrogen, and carbon monoxide is washed with a stream of liquid nitrogen to remove the carbon monoxide completely and a mixture of hydrogen and nitrogen results. By treatment with liquid nitrogen under pressure at —180° C. all impurities liquefiable at that temperature (hydrogen sulphide, carbonyl sulphide and the last traces of carbon monoxide) can be removed from hydrogen from water gas.[199]

Bronn and Fischer[200] pretreated the gases at a temperature of —60° C., by washing them at a relatively low pressure with liquid ammonia and an organic solvent for acetylene (acetone). To remove the washing liquid, further cooling to —90° C. may be used.

REMOVAL OF HYDROCARBONS

The high solubility of methane and gaseous hydrocarbons generally in kerosene, gas oil, and other petroleum fractions is well known and it is possible to eliminate hydrocarbons almost completely by scrubbing with such liquids at appropriate pressures. To eliminate hydrocarbons from hydrogen it has been proposed to wash the gas with benzine under pressure at a temperature below —60° C. but above the freezing point of the solvent.[201] According to Gordon and Hughes,[202] methane may be eliminated from mixtures containing hydrogen and hydrocarbons by washing the gas under 250 atmospheres with a high-boiling solvent such as kerosene.

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[197] Gesellschaft für Lindes Eismaschinen, British Patent 7,205, 1911; *Chem. Abs.*, 1912, **6**, 2517; British Patent 9,260, 1911; *Chem. Abs.*, 1912, **6**, 2826; Swiss Patent 56,594, 1911; *Chem. Abs.*, 1913, **7**, 2670; German Patent 261,735, 1911; *Chem. Abs.*, 1913, **7**, 3645. *Cf.* Claude, U. S. Patent 1,212,455, Jan. 16, 1917; assigned to Soc. l'Air Liquide (Soc. Anon. pour l'étude et l'exploitation des procédés G. Claude); *J.S.C.I.*, 1917, **36**, 330. French Patents 475,297 and 475,346, 1914; *J.S.C.I.*, 1916, **35**, 31.

[198] *Z. angew. Chem.*, 1929, **42**, 760; *Chem. Abs.*, 1929, **23**, 4798; *Brit. Chem. Abs.* **B**, 1929, 766.

[199] Lefort des Ylouses, *Science ind.*, 1927, 11, 53; *Chem. Abs.*, 1929, **23**, 2536.

[200] U. S. Patent 1,774,633, Sept. 2, 1930; *Chem. Abs.*, 1930, **24**, 5139; British Patent 318,319, 1928; assigned to Concordia Bergbau A.-G.; *Brit. Chem. Abs.* **B**, 1929, 969; see Bronn, *Z. angew. Chem.*, 1929, **42**, 760; *Chem. Abs.*, 1929, **23**, 4798.

[201] British Patent 299,167, 1927; *Brit. Chem. Abs.* **B**, 1929, 45.

[202] British Patent 304,345, 1927; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 233; *cf.* Hughes, British Patent 293,138, 1927; assigned to Synthetic Ammonia and Nitrates, Ltd.; *Brit. Chem. Abs.* **B**, 1928, 670.

Removal of Carbon Monoxide

A number of methods have been suggested for removing carbon monoxide from mixtures with hydrogen, for example, from water gas or the gas obtained by treating methane with steam or carbon dioxide at high temperatures (see Chapter 10). Bosch and Wild[203] proposed to remove traces of carbon monoxide by passing the gases through sodium hydroxide at high temperatures and pressures. For example, hydrogen containing 1 per cent of carbon monoxide is treated with an 80 per cent solution of sodium hydroxide under 50 atmospheres pressure at 260° C. or with a 25 per cent solution under 200 atmospheres at 240° C.

Carbon monoxide can be absorbed in an ammoniacal solution of a cuprous salt, the method usually used in gas analysis.[204] Huntington[205] proposed to remove carbon monoxide from producer gas by using this absorbent and applying pressure to the gas. The copper solution is regenerated by subjecting the absorbent to a vacuum. Williams[206] and Linde[207] have described similar procedures. Ueno and Kimura[208] treated by-product hydrogen with metallic copper, a cuprous salt and ammonium hydroxide.

The Badische Company[209] used ammoniacal solutions of cuprous chloride under pressures above 100 atmospheres for the absorption but later recommended the use of solutions with excess ammonia[210] or of ammoniacal solutions of cuprous formate or acetate[211] to overcome some of the corrosive action on the iron vessels employed. DeJahn[212] suggested cuprous carbonate. Gordon and Hughes[213] eliminated carbon monoxide and unsaturated hydrocarbons from gas mixtures with an ammoniacal cuprous solution using pressures of 100 to 250 atmospheres.

Frank,[214] in various processes, proposed to conduct previously dried water gas over calcium carbide maintained at a temperature between 300° C. and the melting point of the carbide to separate pure hydrogen. Under these conditions the impurities present in the hydrogen, according to Frank, reacted as indicated below:

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[203] U. S. Patent 1,126,371, Jan. 26, 1915; *Chem. Abs.*, 1915, **9**, 697; U. S. Patent 1,133,087, Mar. 23, 1915; *Chem. Abs.*, 1915, **9**, 1227; both patents assigned to Badische Anilin- und Soda-Fabrik. Badische Anilin- und Soda-Fabrik, British Patent 1,759, 1912; *J.S.C.I.*, 1912, **31**, 1180; British Patent 14,509, 1913; *J.S.C.I.*, 1914, **33**, 256; French Patent 439,262, 1912; *J.S.C.I.*, 1912, **31**, 722.

[204] A study of carbon monoxide absorption in ammoniacal cuprous carbonate solutions has been made by Hainsworth and Titus, *J.A.C.S.*, 1921, **43**, 1. See Chapter 49.

[205] British Patent 15,310, 1885; *J.S.C.I.*, 1885, **4**, 737.

[206] British Patent 19,096, 1889; *J.S.C.I.*, 1891, **10**, 270.

[207] Gesellschaft für Lindes Eismaschinen A.-G., German Patent 289,106, 1914; *Chem. Abs.*, 1916, **10**, 2508.

[208] Japanese Patent 31,292, 1917; *Chem. Abs.*, 1918, **12**, 208.

[209] Badische Anilin- und Soda-Fabrik, German Patent 282.505, 1913; *Chem. Abs.*, 1915, **9**, 2299.

[210] Gaus, U. S. Patent 1,196,101, Aug. 29, 1916; assigned to Badische Anilin- und Soda-Fabrik; *Chem. Abs.*, 1916, **10**, 2624; British Patent 8.030, 1914; *Chem. Abs.*, 1915, **9**, 2575.

[211] Badische Anilin- und Soda-Fabrik, British Patent 9.271, 1914; *Chem. Abs.*, 1915, **9**, 2801; British Patent 20,616, 1914; *Chem. Abs.*, 1916, **10**, 956; Dutch Patents 1,273 and 1,274, 1916; *Chem. Abs.*, 1916, **10**, 1779; German Patent 288,450, 1914; *Chem. Abs.*, 1916, **10**, 2397; German Patent 289,694, 1914; *Chem. Abs.*, 1916, **10**, 2624; German Patent 288,843, 1914; *Chem. Abs.*, 1916, **10**, 2982; Austrian Patent 72,240, 1916; *Chem. Abs.*, 1917, **11**, 873.

[212] British Patent 120,546, 1918; assigned to General Chemical Co.; *Chem. Abs.*, 1919, **13**, 643.

[213] British Patent 304,345, 1927; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 233.

[214] German Patent 174,324, 1905; *Chem. Abs.*, 1907, **1**, 804; German Patent 177,703, 1903; *Chem. Abs.*, 1907, **1**, 1212; British Patent 26,808, 1906; *J.S.C.I.*, 1907, **26**, 1091. U. S. Patent 873,853, Dec. 17, 1907; *Chem. Abs.*, 1908, **2**, 1201. U. S. Patent 964,415, July 12, 1910; *Chem. Abs.*, 1910, **4**, 2726. British Patent 26,928, 1906; *Chem. Abs.*, 1907, **1**, 1797. French Patent 371,814, 1906; *Chem. Abs.*, 1908, **2**, 2606. See *J. Gasbel.*, 1908, **51**, 48; *Chem. Abs.*, 1908, **2**, 1337.

$$CO + CaC_2 \longrightarrow CaO + 3C$$
$$CO_2 + 2CaC_2 \longrightarrow 2CaO + 5C$$
$$3CO_2 + 2CaC_2 \longrightarrow 2CaCO_3 + 5C$$
$$O + CaC_2 \longrightarrow CaO + 2C$$
$$2N + CaC_2 \longrightarrow CaN_2C + C$$

Williams[215] proposed to convert carbon monoxide present into methanol, which can then be removed by cooling the gases under pressure. Hydrogen containing 2 to 10 per cent of carbon monoxide is passed under a pressure of 900 atmospheres over a catalyst at 400° C. The catalyst is made by heating zinc carbonate or a mixture of zinc and chromic hydroxides. Methanol is formed from carbon monoxide thus.[216]

$$CO + 2H_2 \longrightarrow CH_3OH$$

REMOVAL OF CARBON DIOXIDE

Removal of carbon dioxide from gas mixtures is relatively easy. Conversion of carbon monoxide to carbon dioxide can be effected with steam in the presence of certain catalysts, according to the reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

This reaction is reversible and unless steps are taken to remove the carbon dioxide as it is formed, the resulting gas mixture contains carbon monoxide, carbon dioxide and hydrogen in such proportions that further purification becomes difficult and expensive. Lime and other alkaline contact materials have been suggested for absorbing the carbon dioxide as it is formed.[217] From the work of Engels[218] and others, it appears that the best temperature for this exothermic reaction, which is actively catalyzed by metallic oxides (iron oxide), is 400° to 600° C. Many processes for effecting this conversion have been developed but only a few salient points of these need be noted, since they have been described elsewhere.[219] The reaction temperature is usually 400° to 600° C. and the oxides or iron, cobalt, and nickel dispersed on non-metallic supports have been recommended as catalysts.[220] Other suggested contact materials contain active substances, especially oxygen compounds of copper, chromium, manganese, magnesium, thorium, uranium, beryllium or antimony.[221]

The use of lime water under pressure has also been suggested for washing gases for the removal of carbon dioxide.[222] Gordon and Hughes washed out carbon dioxide, hydrogen sulphide and sulphur compounds with solutions containing ammonia under pressures from 100 to 250 atmospheres.[228] Scrubbing with water under pressures up to 200 atmospheres has also been proposed by Gordon,[224] who subsequently released the pressure to 20 atmospheres to obtain gas richer in hydrogen, leaving gases richer in carbon dioxide in solution. He effected further separation by repeating the process.

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[215] British Patent 258,887, 1926; assigned to Lazote, Inc.; *Brit. Chem. Abs.* **B**, 1928, 230.

[216] Other processes for the conversion of carbon monoxide to methanol are given by Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, **1930**, 652-691.

[217] See, for example, Mond and Langer, British Patent 12,608, 1888; *J.S.C.I.*, 1889, **8**, 767; duMotay, U. S. Patents 229,338, 229,339 and 229,340, June 29, 1880. Ellenberger, U. S. Patent 989,955, Apr. 18, 1911; assigned to Chemische Fabrik Griesheim-Elektron; *Chem. Abs.*, 1911, **5**, 2325. Siedler and Henke, U. S. Patent 1,181,264, May 2, 1916; *Chem. Abs.*, 1916, **10**, 1708. Ellis, U. S. Patent 1,173,417, Feb. 29, 1916; *Chem. Abs.*, 1916, **10**, 1083. Goold-Adams and Greenwood, British Patent 137,340, 1918; *J.S.C.I.*, 1920, **39**, 232A.

[218] Dissertation, Karlsruhe, 1911; *J. Gasbel.*, 1919, **62**, 477, 493. Levi and Piva, *Ann. chim. appl.* 1914, **1**, 1; *J.S.C.I.*, 1914, **33**, 310; *Chem. Soc. Abs.*, 1916, **110** (2), 525. Evans and Norton, *Ind. Eng. Chem.*, 1926, **18**, 513.

[219] Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, **1930**, 728; Taylor, "Industrial Hydrogen," Chemical Catalog Co., Inc., New York, **1921**, 60; Marek and Hahn. "The Catalytic Oxidation of Organic Substances in the Vapor Phase," Chemical Catalog Co., Inc., New York, **1932**, 110.

[220] Soc. l'air liquide (Soc. anon. pour l'étude et l'exploitation des procédés G. Claude), French Patent 471,162, 1913; *J.S.C.I.*, 1915. **34**, 163; British Patent 15,053, 1914; J.S.C.I., 1915, **34**, 786.

[221] Larson, British Patent 311,737, 1928; *Chem. Abs.*, 1930, **24**, 929; Beekley, Canadian Patent 284,584, 1928; *Chem. Abs.*, 1929. **23**, 1225; both patents assigned to Lazote, Inc.

[222] See, for example, Bosch and Wild, U. S. Patents 1,113,096 and 1,113,097, Oct. 6, 1914; assigned to Badische Anilin- und Soda-Fabrik; *Chem. Abs.*, 1914, **8**, 3841. U. S. Patent 1,115,776,

To absorb carbon dioxide from gases such as those formed in the reaction of hydrocarbons with steam (see Chapter 10), Al [225] treated them with an excess of steam (above an equimolecular proportion with respect to the carbon dioxide) in the presence of a solid alkali carbonate at a temperature above the condensing temperature of steam.

Nov. 3, 1914; *Chem. Abs.*, 1915, **9**, 129; U. S. Patent 1,157,669, Oct. 26, 1915; *Chem. Abs.*, 1916, 9. 3335; U. S. Patent 1,200,805, Oct. 10, 1916; *Chem. Abs.*, 1916, **10**, 3142; all three patents assigned to Badische Anilin- und Soda-Fabrik. Heissler, U. S. Patent 1,672,528, June 5, 1928; assigned to Atmospheric Nitrogen Corp.; *Chem. Abs.*, 1928, **22**, 2644. Mond and Langer, British Patent 12,608, 1888; *J.S.C.I.*, 1889, **8**, *767*.

[223] British Patent 304,345, 1927; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 233.

[224] British Patent 311,299, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 557.

[225] U. S. Patent 1,831,731, Nov. 10, 1931; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, **26**, 813.

Chapter 8

The Carbon Black Industry. Deposition of Carbon from Flames

The industry classifies blacks, which consist of substantially pure carbon, roughly into two divisions, namely (1) carbon black, which is made by impingement of a flame of hydrocarbon gas (usually natural gas) on a surface (generally metallic); and (2) lampblack which is deposited as a soot in the incomplete combustion of a solid or liquid carbonaceous substance in free space (i.e., without impingement).[1] Carbon black is more finely divided than lampblack and for this reason is generally regarded as superior for use in rubber compounding, especially tire tread stock.

This division of blacks into two classes, carbon black and lampblack, depending upon the method of deposition, is by no means a satisfactory one, and a classification based on methods of manufacture would be more explicit and, for the present purpose, more satisfactory. Five such methods have been listed by Chamberlin and Rose:[2]

1. *Incomplete Combustion with Impingement.* A hydrocarbon gas, burning in a limited supply of air, is allowed to impinge on a cool depositing surface. The earliest methods for the manufacture of carbon black from natural gas, such as the so-called channel, disc, roller, and plate processes which will be described in this chapter, were of this type. In point of production these are the most important.

2. *Thermal Decomposition.* A hydrocarbon gas or atomized oil is subjected to thermal decomposition in the absence of air. In this class would fall the "Thermatomic" and other processes described in Chapter 7 for the production of hydrogen and carbon.

3. *Explosion.* A hydrocarbon gas such as acetylene is exploded in a limited supply of air, resulting in decomposition to carbon. Some examples of this class have already been discussed in Chapter 7 and others will be found in Chapter 9.

4. *Incomplete Combustion without Impingement.* A liquid or solid hydrocarbon is burned in a limited supply of air to produce soot which is collected. Lampblack is manufactured in this way. Some processes of this type have been mentioned in Chapter 7.

5. *Destructive Distillation.* Destructive distillation of organic materials produces various kinds of charcoals and cokes (e.g., petroleum coke) which are subsequently pulverized for use.

In Chapter 7 the methods of decomposing hydrocarbons to produce carbon and hydrogen (classes 2, 3, 4, and 5 above) were discussed. In this chapter the principal emphasis will be placed on those procedures in which the hydrocarbons, generally natural gas, are burned with a flame in an insufficient supply of air (class 1 above). From a consideration of the mechanism of this latter process it has been shown that it, too, is a simple decomposition effected by the heat produced by combustion of part of the gas.

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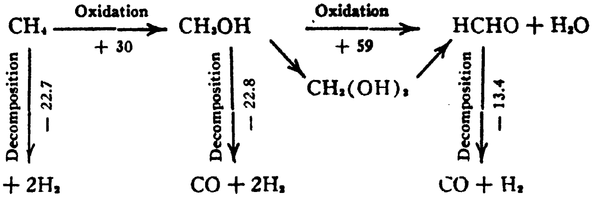
[1] *Cf.* Cabot, *Reports Eighth Intern. Congress Applied Chem.*, 1912, **12**, 13. Neal, *U. S. Bur. Mines Bull.* **192**, 1922, 1. Wiegand, *Ind. Eng. Chem.*, 1931, **23**, 178.

[2] *Trans. Am. Inst. Chem. Eng.*, 1929, **22**, 155.

MECHANISM OF CARBON BLACK FORMATION

The production of carbon black by incomplete combustion of gases containing hydrocarbons is not the result of a preferential combustion of the hydrogen of the hydrocarbon but is a direct thermal decomposition. Part of the gas burns producing oxides of carbon, and the heat liberated is sufficient to cause the decomposition of another part of the hydrocarbon gas into carbon and hydrogen. According to Bone and his collaborators[3] the various processes taking place during the combustion of methane can be formulated as follows:



The thermal relationships are indicated in kilogram calories per mole.

Bone[4] and his collaborators, as previously pointed out in Chapter 7, found that the thermal decomposition of methane is a purely surface effect giving rise to a hard graphitic carbon, but the decomposition of ethane, ethylene, and higher gaseous hydrocarbons takes place throughout the entire mass of the gas, leading to a soft form of carbon. It is well known that unsaturated hydrocarbons, such as ethylene and acetylene, can be formed by incomplete combustion of methane or its homologues and consequently (see Chapter 4) there is a possibility that these unsaturated hydrocarbons, and not methane itself, are the generators of the finely divided carbon black.

The function of the metal surface for deposition is twofold.[5] In the first place the liberated carbon is cooled somewhat so that no oxidation changes, or an agglomeration of particles, from too prolonged heating can take place. Secondly, it allows the carbon to be maintained at a high enough temperature for sufficient time to free it from empyreumatic substances. Too cold a metal surface prevents the maximum separation of carbon and too hot a surface causes loss of carbon by agglomeration. The temperature of the depositing surface should normally not exceed 500° C.[6]

When carbon is maintained at high temperatures for any length of time its physical and chemical properties tend to change markedly. An agglomeration of particles takes place followed by the formation of hard gritty lumps somewhat of the nature of graphitic carbon. To obtain the best quality of carbon black it is essential to avoid the prolonged action of heat on the carbon black initially formed.

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[3] Bone, Davies, Gray, Henstock, and Dawson, *Phil. Trans. Roy. Soc., London*, 1915, (A), 215, 275; *Chem. Soc. Abs.*, 1915, 108 (2), 684; *Chem. Abs.*, 1915, 9, 2976; Bone and Townend, "Flame and Combustion in Gases," Longmans, Green and Co., New York, 1927, 387, 413, 381. See also Perrott and Thiessen, *Ind. Eng. Chem.*, 1920, 12, 324; and Chapter 37.

[4] *Loc. cit.* *Cf.* Bone and Coward, *J.C.S.*, 1908, 93, 1197.

[5] See Perrott, *U. S. Bur. Mines Bull.* 192, 1922.

[6] This was also confirmed later by the work of Plummer and Keller (*Ind. Eng. Chem.*, 1930, 22, 1209), who found that the optimum temperature of the depositing surfaces for the production of gas black from propane was about 516° C.

Wiegand[7] has studied the characteristics of two types of flames, namely, a round and a flat or "batwing" type in black production, and the factors which influence quality and yields. Comparison of products from the two flames revealed that the carbon black obtained from a round flame was characterized by a grayer color, lower oil absorption and absorptive activity, increased flow characteristics, greater miscibility in rubber but diminished reenforcing effects in rubber composition.

Measurements of the temperature of flames of hydrocarbon gases have been made by Loomis and Perrott[8] and Jones, Lewis, Friauf, and Perrott.[9] The flame temperature is markedly affected by the proportion of combustible gas and air in the mixture, of course. The flame temperature reaches a maximum when the mixture contains combustible gas slightly in excess of that necessary to consume all the oxygen present. The observed maximum temperatures obtained with methane, Pittsburgh natural gas, ethane, butane, isobutane, propane, butylene, propylene and ethylene increased in that order from 1880° to 1975° C. Thus, unsaturated hydrocarbons produce higher maximum flame temperatures than saturated ones. These maximum flame temperatures were found to occur over very narrow ranges of gas-air ratios.

DEPOSITION OF CARBON FROM NATURAL GAS FLAMES

Since natural gas varies widely in composition (see Chapter 1), a difference in the yield and quality of the blacks manufactured from gas from various sources is to be expected. Natural gas frequently contains nitrogen, oxygen, hydrogen sulphide, and water vapor as well as carbon dioxide. Indeed only small proportions of hydrocarbons may be present in the raw gas, in such rare cases as certain wells in Mexico[10] and New Mexico,[11] and in a number of other places[11a] which discharge gas consisting largely of carbon dioxide. The relative proportions of the gaseous paraffin hydrocarbons present in natural gases are of special importance in black manufacture. In general, as will be pointed out later, a gas containing a moderate content of ethane is better than one which is almost entirely methane. West Virginia with its supply of gas high in ethane is a particularly favorable location in this respect.

The yield of carbon black varies from one-half to about two pounds per thousand cubic feet of natural gas.[12] This variation in yield depends mainly upon the process used and the type of product desired and is only slightly affected by the character of the gas. Since 31.82 pounds of carbon and 2000 cubic feet of hydrogen are theoretically obtainable from one thousand cubic feet of methane, the process of producing carbon black must be regarded as wasteful. Many a chemist, calculating the theoretical yield of carbon, feels that he is called upon to make an effort in the cause of conservation, and perhaps, what is more important, to produce carbon black at a lower cost.

That the carbon made by burning artificial gas in a limited supply of air could be used to impart to ink a very glossy and intense black was known to certain manufacturers of printing ink as early as 1864.[13] The first factory [14] for the successful commercial production of carbon black from natural gas was erected in 1872. At this plant at New Cumberland, W. Va., the well was connected to a gas holder, from which the gas passed through pipes to gas jets arranged in the same horizontal plane beneath slabs of soapstone pierced by a number of orifices; these apertures permitted the passage of excess smoke and waste gas. The slabs were covered by a domed roof, provided with a damper for controlling ventilation. Transverse horizontal scrapers below the slabs were supported and travelled in horizontal grooves cut in the lower and opposite sides of the dome. The deposited carbon which was removed by these scrapers then fell into sheet-iron troughs. The depositing surface was kept cool by pans through which water was allowed to circulate continuously. This plant produced a carbon black which was inferior in some properties to the product made from artificial gas. It was subsequently shown that the dome was superfluous, that cast iron was better than soapstone as a depositing surface, and that no beneficial results attended the use of air or water for reducing the temperature of the cooling surfaces.

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[7] *Ind. Eng. Chem.*, 1931, **23**, 178.

[8] *Ind. Eng. Chem.*, 1931, **53**, 869. *Cf.* Jones, Lewis and Seaman, *J.A.C.S.*, 1931, **53**, 3992.

[9] *J.A.C.S.*, 1931, **53**, 869.

[10] Martin, *Ind. Eng. Chem.*, 1931, **23**, 256.

[11] *Ind. Eng. Chem., News Edition*, 1931, **9**, 316.

[11a] For sources of natural carbon dioxide in Belgium, see Guilleaume, *Rev. universelle mines*, 1926, (7) **10**, 169; *Chem. Abs.*, 1926, **20**, 2728.

[12] See Perrott, *U. S. Bur. Mines Bull.* **192**, 1922, 53.

[13] See Neal and Perrott (*loc. cit.*) and Cabot (*loc. cit.*, also *J.S.C.I.*, 1894, **13**, 128). The history, manufacture, uses and testing of carbon blacks have also been discussed briefly by Cranor and Venuto (*Am. Paint J.*, 1931, **15**, No. 26, 21).

Certain mechanical improvements, particularly in the design and operation of the scraping device, took place at this stage. At Gambier, Ohio,[15] a competing plant was built with a maximum production capacity of 125 pounds per day, which brought about a great reduction in the price of carbon black. A considerable advance was made in 1883 by L. Martin and Co. in a small plant at Foster Mills, Pa. Here five plates, 24 feet in diameter, cast in segments and supported by a central mast rotating with them, were used for deposition of the carbon black. Beneath these plates were fixed stationary burners. In the same year Blood [16] devised the *rotating disc process,* using plates of only 3 feet diameter as depositing surfaces. The advantage of this was that ventilating holes were unnecessary and the plates could be made in one casting. Beneath each plate, which was revolved by a ratchet at the center, was a scraper in the center of a radial hopper, through which the deposit fell into a longitudinal conveyer.

Hallock and Blood [17] proposed and later started the manufacture of carbon black by the so-called *roller process.* A burner with a small hole in the top, giving a rounded flame, was so placed that its flame impinged on a cast-iron roller (hence, the name of the process) rotating at slow speed. Although only a small yield of carbon black, generally of inferior color, was produced, the black possessed certain advantages which have prevented the complete abandonment of the method. The chief uses of this black are in making lithographic and embossing inks and printing ink for half-tone engravings.

These methods of manufacturing carbon black have been almost entirely superseded (except for small quantities of special blacks) by the *channel process,* which was first employed by McNutt [18] in 1892 in a factory erected at Gallagher, Pa. In this process, a system of channel beams turned with the flat side downwards over a horizontal row of stationary burners was given a slow reciprocating motion. The black was scraped off and removed by a spiral conveyer. Channel irons gave a smoother depositing surface than that of unsurfaced cast-iron plates.

The carbon black deposited on channels may be selectively removed and that deposited on the central longitudinal part of the face of the channels collected separately. According to Wiegand,[19] the carbon deposited at different portions of the channels has varying properties.

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[14] This was the plant of Howarth and Lamb. See Howarth, U. S. Patent 131,446, Sept. 17, 1872; Reissue 6,937, Feb. 22, 1876; and U. S. Patent 161,039, March 23, 1875. For a bibliography and résumé of earlier patents see Neal and Perrott (*loc. cit.*) and Cabot (*loc. cit.*).

[15] This was the plant of Peter Neff which operated for about 10 to 12 years. A large number of patents have been granted to Neff and Fales, most of which Neal and Perrott (*loc. cit.*) have stated to be useless and impracticable.

[16] See A. R. Blood, B. H. Blood, and E. R. Blood, U. S. Patent 387,487, Aug. 7, 1888.

[17] Hallock and E. R. Blood, U. S. Patent 205,955, July 16, 1878. See also E. R. Blood, U. S. Patent 269,378, Dec. 19, 1882.

[18] U. S. Patent 481,240, Aug. 23, 1892.

At about this time an attempt to manufacture carbon black by burning petroleum vapors, or gas enriched by oil vapor, was made by Dysart [20] and Cabot [21] but the use of the product was limited on account of the presence of hard carbon particles. In 1902 a plant was built in West Virginia in which the black obtained by the incomplete combustion of natural gas was collected upon a hollow channel iron, through which a blast of air was blown to cool the depositing surface and to increase the yield of black, but this process has since been abandoned.

From about 1912 onwards attempts were made to produce carbon black by the thermal decomposition of hydrocarbons at high temperatures, already described in Chapter 7. Numerous advances in the incomplete combustion of natural gas have also been made in the meantime.

Martin [22] obtained an increased yield of carbon black by preheating natural gas to 200°-500° C. before burning. Lewis [23] has suggested cooling a portion of the flame separately from the action of the surface by a metal wire or rod passing through it. An enclosure having heat-insulating walls has also been proposed by Lewis [24] to retard the radiation of heat from the plate and flame.

An electrical method of operating a carbon black plant was suggested by Thieme.[25] He connected the positive terminal of a 110-volt direct current electric circuit to a straight iron wire which passed through a luminous gas flame and placed above this wire an iron wire gauze connected to the negative terminal. Lampblack "grows" on the gauze and as soon as the deposit is large enough to come in contact with the straight wire an electric circuit is established. A small magnet connected in series is activated by this circuit, drawing the gauze suddenly sideways and shaking off the lampblack. The circuit is thus broken and the process repeated. A very fine carbon, free from lumps, was obtained. The same result was observed when the terminals were connected to an induction coil so that a short spark passes between them.[26]

Since carbon is an incomplete combustion product of hydrocarbons efforts have been made to secure better yields by stifling the flame in some way, for example, by mixing an inert gas such as nitrogen or carbon dioxide with the hydrocarbon gas.[27]

Lewis [28] has suggested the exposure of the flame and iron depositing surface to ultraviolet light to increase the yield of carbon black in impingement processes.

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[19] U. S. Patent 1,809,290, June 9, 1931; *Chem. Abs.*, 1931, **25**, 4368.

[20] U. S. Patent 343,446, June 8, 1886.

[21] U. S. Patent 491,923, Feb. 14, 1893.

[22] U. S. Patent 1,477,511, Dec. 11, 1923; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1924, **18**, 573.

[23] U. S. Patent 1,510,485, Oct. 7, 1924; *Chem. Abs.*, 1924, **18**, 3688.

[24] U. S. Patent 1,881,084, Oct. 4, 1932; assigned to Columbian Carbon Co.; *Chem. Abs.*, 1933, **27**, 574.

[25] *Z. Elektrochem.*, 1912, **18**, 131; *Chem. Abs.*, 1912, **6**, 1098; German Patent 256,675, 1912; *Chem. Abs.*, 1913, **7**, 2111; *Z. physik. Chem.*, 1915, **89**, 693; *Chem. Abs.*, 1915, **9**, 2347.

[26] *Z. physik. Chem.*, 1912, **78**, 490; *Chem. Abs.*, 1912, **6**, 1706. See also *Elektrochem. J.*, 1913, **20**, 61; *Chem. Abs.*, 1913, **7**, 3278.

[27] See, e.g., Rumbarger, U. S. Patent 1,401,737, Dec. 27, 1921; assigned to Southern Carbon Co.; Matlock, U. S. Patent 1,438,542, Dec. 12, 1922; assigned to Monroe-Louisiana Carbon Co.; Lewis, U. S. Patent 1,418,811, June 6, 1922, assigned to the Goodyear Tire and Rubber Co.; *Chem. Abs.*, 1922, **16**, 2760; Darrah, U. S. Patent 1,448,655, Mar. 13, 1923; Matlock, U. S. Patent 1,458,351, June 12, 1923; assigned to Monroe-Louisiana Carbon Co.; Matlock, U. S. Patent 1,508,367, Sept. 9, 1924; assigned to Monroe-Louisiana Carbon Co.; Bonnington, U. S. Patent 1,515,333, Nov. 11, 1924; Messenger, U. S. Patent 1,577,481, Mar. 23, 1926, assigned to Standard Oil Development Co. See Chapter 7.

[28] U. S. Patent 1,811,889, June 30, 1931; assigned to Columbian Carbon Co.; *Chem. Abs.*, 1931, **25**, 4983.

An apparatus in which an electric current is passed through a flame from which carbon black is being deposited has also been described by Lewis.[29]

Minchin and Downer [30] used two conductors for the deposition of carbon, one of which may be rotated and from which the carbon may be continuously removed and the other, forming the burner, is charged with alternating or direct current and held in the flame of the burning hydrocarbon. In this process the yields are increased by removal of the carbon deposit, by maintaining a uniform temperature, or by cooling.

An apparatus with thermostatic control for producing lampblack by the combustion of materials such as natural gas has been described by Rumbarger.[31]

Wiegand and Venuto [32] agglomerated carbon black, making it less bulky and dusty, by wetting it with water, bringing it into contact with gasoline to displace substantially all the water, and finally evaporating the gasoline. Rubber-compounding ingredients may be added to the black during the process and pellets may be formed.

The spraying of water into the fumes from the partial combustion of natural gas has been recommended by Lewis.[33] The water washes out all the free carbon and condenses the water vapor formed in the combustion. The carbon particles thus deposited are separated from the water.

Yields of carbon black higher than those obtainable by burning a hydrocarbon gas with a continuous flame were produced when the gas was burned in an atmosphere of compressed air. Francis [34] has shown that the yield of high-grade carbon black can be trebled, for example, at 100 pounds pressure. In this work the very great theoretical and practical significance of the upper limit of inflammability of the hydrocarbon gas in luminous flames is clearly demonstrated. At atmospheric pressure the upper limit of inflammability of methane in air is about 14 per cent. Such a mixture contains 18 per cent of oxygen, an amount more than sufficient to combine with all the carbon present in the methane according to the reaction:

$$(1)\ CH_4 + O_2 \longrightarrow CO + H_2 + H_2O$$

The low yields usually obtained are due therefore to the fact that an excess of oxygen for equation (1) is present.

Small amounts of carbon are formed by the side reaction:

$$(2)\ CH_4 + O_2 \longrightarrow C + 2H_2O$$

The relative amounts oxidized according to (1) and (2) are determined by the relative excess of oxygen at some critical point in the flame and by the equilibrium between the products:

$$(3)\ C + H_2O \rightleftharpoons CO + H_2$$

It is obvious, therefore, that to effect an appreciable increase in the yield of carbon, conditions must be so changed as to diminish the excess of oxygen in the flame by raising the upper inflammability limit of the hydrocarbon or by shifting the equilibrium (3) to the left. From the results of Jones,[35] Francis has shown that the addition of inert gases or vapors to stifle the flame as proposed by some is futile.

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[29] U. S. Patent 1,881,085, Oct. 4, 1932; assigned to Columbian Carbon Co.; *Chem. Abs.*, 1933, **27**, 574.

[30] Burmah Oil Co., Ltd., British Patent 357,133, 1930; *Brit. Chem. Abs.* **B**, 1931, 1129.

[31] U. S. Patent 1,797,368, March 24, 1931; assigned to Imperial Oil and Gas Products Co.; *Chem. Abs.*, 1931, **25**, 2839.

[32] British Patent 327,979, 1929; *Chem. Abs.*, 1930, **24**, 5118; Canadian Patent 301,071, 1930; *Chem. Abs.*, 1930, **24**, 3866.

[33] U. S. Patent 1,801,436, April 21, 1931; assigned to Columbian Carbon Co.; *Chem. Abs.*, 1931, **25**, 3447.

[34] *Ind. Eng. Chem.*, 1931, **23**, 612; U. S. Patent 1,820,657, Aug. 25, 1931; assigned to Magnolia Petroleum Co.; *Brit. Chem. Abs.* **B**, 1932, 490.

The upper limit of inflammability of methane in air increases with increased pressure in the manner illustrated in Table 49.[36]

Table 49.—*Effect of Pressure upon Upper Inflammability Limit of Methane in Air.*

Pressure (atmos.)	1	10	50	125
Per cent methane	13.5	17.0	29.5	45.4

From this it might be expected that by increasing the air pressure around the luminous flame better yields of carbon would be obtained, as Francis proved by direct experiments. By burning gas flames in air under pressures of the order of 12 to 14 atmospheres, he obtained yields of black of 7 to 8.5 per cent (1 pound per 1000 cu. ft. of methane = 3% yield), a decided increase over processes operating at atmospheric pressure. The carbon produced in these experiments was equal in tinting power and apparently identical with the best grades of carbon black on the market.

Francis has also calculated the flame equilibria in a methane-air flame at various pressures and at 437° C. (the temperature giving results most closely in agreement with observed yields) with the results given in Table 50.

Table 50.—*Calculated Yields of Carbon in Equilibrium at 437° C. in a Methane Flame.*

Pressure in Atmos.	Upper Inflammability Limit, CH_4	Yield of Carbon
	Per Cent	
1	13.5	2.93
2	14.1	8.75
5	15.3	16.15
10	17.0	23.1
20	20.5	28.8
30	23.5	32.3
34	24.8	32.7
40	26.5	32.2
60	32.0	30.2
125	45.4	21.6

The calculated percentage yield of carbon increases rapidly with increasing pressure up to about 34 atmospheres and then declines gradually. This decrease is due to the increasing amounts of methane which are prevented from decomposing by the effect of high pressures upon the equilibrium.

With natural gas at its present low price the yield of black is not economically important. It is probably cheaper to burn five times as much gas to produce a given amount of black than to install a process such as the one described above. Nevertheless, as the supplies of gas begin to diminish, methods capable of producing increased yields will take on a new significance, particularly if the black produced by them is of high quality.

Table 51 shows the yield of carbon black produced from natural gas by various processes in different localities, as reported by Neal in 1922.[37]

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[35] *U. S. Bur. Mines. Tech. Paper* 450, 1929.

[36] Bone and Townend, "Flame and Combustion in Gases," Longmans, Green and Co., New York, 1927, 98, 101.

[37] *U. S. Bur. Mines Bulletin* 192, 1922, 37.

TABLE 51.—*Yield of Carbon Black by Various Processes.*

State	Process	Carbon Black Lbs. per 1000 Cu. Ft. of Gas
Louisiana	Channel	0.78
"	"	0.95
"	"	0.80
"	Large Plate	0.80
West Virginia	" "	1.10
" "	Rotary Disc	0.95
" "	Roller	0.80
" "	Rotary Disc	1.00
" "	Channel	1.12
" "	"	1.30
" "	Rotary Disc	1.40
Oklahoma	Channel	1.20
Wyoming	"	1.40

It is interesting to note, however, that the average yield by the channel process since 1922 has not been as low as indicated in the above table. Thus, the average yield for the entire United States in 1929 (about 90 per cent of which was made by the channel process) was 1.40 pounds per thousand cubic feet of gas and this was increased to 1.43 in 1930 and 1.44 in 1931.[38] The thermatomic process (see Chapter 7), in comparison, is capable of giving consistent yields of 7 pounds of carbon black by the thermal decomposition of one thousand cubic feet of natural gas.[39]

The principal factors influencing the yield and quality of the carbon black produced by the incomplete combustion of natural gas, as given by Chamberlin and Rose,[40] are (1) pressure of gas, (2) rate of burning, (3) nature of the burner tip, (4) composition of gas, (5) position of plate in flame, (6) draft conditions, (7) material of plate, (8) motion of plate, (9) shape of plate, (10) humidity of atmosphere, (11) barometric pressure, (12) temperature of gas, (13) temperature of plate, and (14) uniformity of operating conditions. Dependent upon some or all of the above factors are (a) the height of the flame, and (b) the composition and (c) temperature of the atmosphere in which the flame burns. Burner tips made of lava, a selected steatite, are generally favored in the industry.[41]

Regulation of the air supply is controlled more or less empirically, the color of the smoke issuing from the stack being taken as an index. Admission of too much air will, of course, result in too hot a flame and a large proportion of the carbon will be burned, while too little air will give a flame in which the gas will not be decomposed sufficiently and from which little carbon will deposit. Moreover, in the latter case, the carbon produced is likely to be contaminated by intermediate products of combustion. The rate of rotation of the cooling surfaces also affects the quality rather than the yield of carbon black.

The figures in Table 52, reported by Neal,[42] show the influence of the composition of natural gases from various localities on the yields of carbon black produced by the same process (laboratory test simulating channel process) under identical controlled conditions.

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[38] Hopkins and Backus, *Mineral Resources of the United States*, 1929, **2**, 55; likewise report for 1931 published in *Chem. Met. Eng.*, 1932, **39**, 380.

[39] *Chem. Met. Eng.*, 1932, **39**, 380.

[40] *Trans. Am. Inst. Chem. Eng.*, 1929, **22**, 155.

[41] Neal, *U. S. Bur. Mines Bull.* **192**, 1922, 21.

[42] *Loc. cit.*

TABLE 52.—*Yields of Carbon Black from Natural Gas.*

Source	Louisiana	West Virginia	West Virginia	Wyoming
Composition of Gas				
Methane, %	94.12	70.75	65.23	46.45
Ethane, %	3.44	24.14	30.07	43.10
Carbon dioxide, %	0.50	0.28	1.56	0.96
Nitrogen, %	1.94	4.83	3.14	9.49
Net heating value, B.t.u. per cu. ft.	962	1086	1134	1176
Carbon content, lbs. per 1000 cu. ft	33.8	39.9	42.3	44.3
Carbon yield				
Carbon black obtained, lbs. per 1000 cu. ft.	0.80	1.00	1.10	1.40
Recovery of carbon, %	2.4	2.5	2.6	3.1

In the analyses given in the above table the "ethane" figures probably represent not only ethane but also its immediate higher homologues. The yield of carbon black per 1000 cubic feet of gas, and also the percentage recovery of carbon as carbon black, increase with an increase in the proportions of the homologues of methane in the gas.[43]

Recovery of gasoline from natural gas before utilizing it to manufacture carbon black is a large source of revenue and does not reduce the carbon black yield to an appreciable extent.[44]

Sulphur compounds when present in the gas, accumulate on the lava tips, thus decreasing the volume of gas passed through the burner and causing the flame to fork and produce an uneven distribution of carbon over the depositing surface.

DEPOSITION OF CARBON FROM OTHER HYDROCARBON FLAMES

Carbon black was made as early as 1864 from artificial gas. Since that time a wide variety of gases have been thermally decomposed to yield carbon black and hydrogen (see Chapter 7) but the greatest proportion of commercial production of carbon black has been largely restricted to natural gas as a source because of its cheapness. Some consideration, however, has been given to the burning of other gases as well. For example, Berger and Wirth[45] burned acetylene to make acetylene black. Plummer and Keller[46] obtained carbon black from propane and studied the effect of various factors on its production from this gas by the channel system. The product was equal in quality to that made from methane. The conditions of operation using propane or methane show a close agreement and demonstrate the essential identity of the basic flame reactions of the two gases. The partial combustion of diacetylene or a substitution product in a special burner has also been proposed.[47]

Kroch[48] suggested the enriching of natural gas or methane with ethylene or ethane for the production of carbon black. Vaporized oil is added to the gas mixture and this is subsequently cracked and burned in a limited supply of air. The incomplete combustion of heavy oil distillates cracked under low pressure has also been proposed.[49]

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[43] This is supported by the later work of Plummer and Keller (*Ind. Eng. Chem.*, 1930, **22**, 1209) on the production of carbon black from propane by what was essentially the channel process. Yields of about 3 lbs. per 1000 cu. ft. of gas were obtained while the results suggested an identity of basic flame reactions with those occurring in normal carbon black production from methane.

[44] See Chapter 1. An absorption process for recovering gasoline from the residual gases of compression plants has been described by Dykema and Neal, *U. S. Bur. Mines Tech. Paper* **232**, 1920.

[45] German Patent 92,801, 1896; *Chem. Zentr.*, 1897, **2**, 688.

[46] *Ind. Eng. Chem.*, 1930, **22**, 1209.

[47] I. G. Farbenindustrie A.-G., British Patent 357,749, 1930; *Brit. Chem. Abs.* **B**, 1931, 1129.

[48] U. S. Patent 1,815,851, July 21, 1931; *Chem. Abs.*, 1931, **25**, 5523. Numerous methods for the enrichment of gases with petroleum oils or for the burning of petroleum oils have been previously suggested. See, for example, Neff and Fales, U. S. Patent 160,786, Mar. 16, 1875; Cabot, U. S. Patent 491,923, Feb. 14, 1893; Dysart, U. S. Patent 343,446, June 8, 1886; Lampblack, Ltd., British Patent 17,223, 1912; Maiser, German Patent 203,711, 1909; Siemens and Co., German Patent 291,727, 1914; Wegelin, U. S. Patent 807,646, Dec. 19, 1905; Neal and Perrott, *U. S. Bur. Mines Bull.* **192**, 1922.

A mixture of 15 to 70 per cent hydrogen and a hydrocarbon gas such as methane has been used by Lewis[50] for the production of carbon black by incomplete combustion in which the flame is allowed to impinge on a collecting surface. Such a mixture is obtained when natural gas, stripped of its heavier constituents, is passed through a tube heated to between 600° and 900° C.[51] At this temperature hydrogen, methane and cyclic hydrocarbons but no free carbon are formed. The cyclic hydrocarbons are removed by condensation before the gas is burned to carbon black. The cyclic hydrocarbons may be retained in the gas by insufficient cooling.[52] In another method by Lewis[52a] for the production of carbon black, a hydrocarbon gas is oxidized with insufficient air in a special burner designed to project alternate layers of hydrocarbon and air, the spacing and rate of flow of which are adjusted to minimize turbulence.

The incomplete combustion of oils to obtain carbon black has also been suggested. Egloff,[53] for example, discharges residual oil from one still into a second still where air is injected into the oil while it is still at a temperature above its flashpoint. An apparatus for burning oil mixtures has also been described by Lewis.[54] The production of lampblack by burning liquid hydrocarbons while flowing in a thin film over an inclined surface of which the temperature is adjusted by a cooling liquid has been suggested by Morrell and Mekler.[54a]

Strout and Lyder[55] admitted air at a number of points to a petroleum oil to effect incomplete combustion. The quantity of air is controlled in such a manner that no additional heating is required. The gaseous waste products, after being freed from carbon, may be used to control the temperature by mixing them with the air.[55a] Beaver[56] burned contiguous flowing streams of hydrocarbons and insufficient air in a heated enclosed chamber to produce carbon black.

Begrov[57] has described an apparatus in which petroleum hydrocarbons may be converted to lampblack. After passing a hydraulic seal, light petroleum fractions are admitted into the upper end of a heated coil consisting of a number of banks, and the vapor which is discharged through perforations at the bottom is burned.

Methods for the direct formation of printer's ink have been described by Miller.[58] In one process 1 part of hydrocarbon oil is decomposed into carbon and gases by incomplete combustion with 5 to 9 parts by weight of air at a temperature between 1093° and 1426° C. The gases are removed rapidly from the zone of reaction at a minimum constant velocity of 500 feet per minute and cooled while at the same speed. The carbon particles are separated from the products of combustion by causing the gases to impinge against a film or sheet of an oily ink vehicle. This oil vehicle is continuously withdrawn, mixed with a fresh quantity of the same vehicle, cooled and again spread into a film for further removal of carbon from the gases. Unabsorbed oil-laden carbon particles can be removed, after reducing the velocity of the gases, by electrical precipitation. Miller and Masson[59] deposited carbon in a liquid base using an apparatus consisting of a number of rotating perforated discs dipping into the liquid. The products of combustion on passing through one disc impinge upon the wetted surface of the next one. Miller[60] produced carbon black by thermally decomposing a portion of the hydrocarbon oil in an inner zone heated by combustion of another portion of the oil in an outer zone. The hydrocarbon oil is continuously supplied to the decomposition zone while the air necessary for the partial combustion enters only the outer zone.

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[49] Thomas Carbon Black Co., British Patent 340,482, 1929; *Brit. Chem. Abs.* **B**, 1931, 330.

[50] U. S. Patent 1,811,854, June 30, 1931; assigned to Columbian Carbon Co.; *Chem. Abs.*, 1931, **25**, 4983. British Patent 309,992, 1929; *Brit. Chem. Abs.* **B**, 1930, 936.

[51] British Patent 309,488, 1929; *Brit. Chem. Abs.* **B**, 1930, 936. See Chapter 7.

[52] U. S. Patent 1,810,918, June 23, 1931; assigned to Columbian Carbon Co.; British Patent 331,821, 1929; *Chem. Abs.*, 1931, **25**, 176.

[52a] U. S. Patent 1,891,202, Dec. 13, 1932; assigned to Goodyear Tire and Rubber Co.; *Brit. Chem. Abs.* **B**, 1933, 851.

[53] U. S. Patent 1,535,214, April 28, 1925; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1925, **19**, 1933.

[54] U. S. Patent 1,838,316, Dec. 29, 1931; *Chem. Abs.*, 1932, **26**, 1402.

[54a] U. S. Patent 1,890,188, Dec. 6, 1932; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 1722.

[55] U. S. Patent 1,872,519, Aug. 16, 1931; assigned to Standard Oil Co. of California; *Chem. Abs.*, 1932, **26**, 6080.

[55a] Lyder, U. S. Patent 1,844,327, Feb. 9, 1932; assigned to Standard Oil Co. of California; *Chem. Abs.*, 1932, **26**, 2024.

[56] U. S. Patent 1,902,753, Mar. 21, 1933; assigned to General Atlas Carbon Co.; *Chem. Abs.*, 1933, **27**, 3299.

[57] Russian Patent 14,204, 1927; *Chem. Abs.*, 1931, **25**, 1045.

[58] British Patent 286,207, 1927; assigned to Ault and Wiborg Co.; *Brit. Chem. Abs.* **B**, 1929, 196; U. S. Patent 1,765,991, June 24, 1930; assigned to Ault and Wiborg Co.; *Chem. Abs.*, 1930, **24**, 4176.

Physical and Chemical Properties of Carbon Black

Ultimate analyses show that carbon blacks contain substances other than carbon.[61] Appreciable proportions of volatile and small proportions of mineral matter are usually present. In good-grade blacks, however, the mineral (ash) content is extremely small. The analyses in Table 53 show the compositions of various carbon blacks used for ink making and of two made by the thermal decomposition of methane. The so-called "long" blacks are used for making the fluid "long" inks (i.e., inks which can be drawn out into a string between the fingers), whereas the "short" blacks produce inks of a buttery consistency which

TABLE 53.—*Analysis of Carbon Black.*[a]

	Long Blacks			Short Blacks			Carbon from Thermal Decomposition of Methane	
	1	2	3	1	2	3	1	2
(1) *Proximate analysis*								
Moisture	3.56	7.13	5.30	2.25	3.02	3.12	0.02	1.25
Volatile matter	11.99	13.41	10.40	5.60	5.48	5.58	0.78	6.40
Fixed carbon	84.40	79.44	84.16	92.13	91.47	91.22	98.36	92.11
Ash	0.05	0.02	0.14	0.02	0.03	0.08	0.84	0.24
(2) *Ultimate analysis on moisture-free basis*								
Hydrogen	0.82	0.57	0.55	0.50	0.52	0.72	0.45	1.13
Carbon	91.42	91.05	92.91	96.96	96.41	96.64	98.72	97.99
Nitrogen	0.04	0.04	0.08	0.09	0.04	0.05	0.01	0.01
Oxygen	7.66	8.26	6.30	2.43	2.69	2.51	—	0.51
Sulphur	0.01	0.06	0.01	0.00	0.31	0.00	0.05	0.12
Ash	0.05	0.02	0.15	0.02	0.03	0.08	0.02	0.24
True specific gravity	1.80	1.78	1.88	1.85	1.80	1.78	—	—

[a] Perrott, *U. S. Bur. Mines Bull.* **192**, 1922.

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[59] U. S. Patent 1,767,089, June 24, 1930; assigned to Ault and Wiborg Co.; *Chem. Abs.*, 1930, **24**, 4362.

[60] U. S. Patent 1,807,321, May 26, 1931; assigned to Ault and Wiborg Co.; *Chem. Abs.*, 1931, **25**, 4096.

[61] This was emphasized by Cabot, *Reports Eighth Inter. Congress Applied Chem.*, 1912, **12**, 13.

do not flow rapidly—the so-called "short" inks.[62] In the former, fluidity is of importance since it permits the ink to be distributed rapidly in thin films over printing surfaces without rupture of these films.

It will be noticed that blacks which are classified as long blacks contain more volatile matter, oxygen, and moisture than the short blacks. When the analytical results are compared it is found that carbon made by decomposing methane at high temperatures (No. 1) is nearly pure carbon. When decomposition is effected at a lower temperature (No. 2) considerable amounts of napththalene and other volatile substances are present. Lampblacks, on the other hand, unless well calcined, invariably contain high proportions of volatile matter (up to 20 per cent). Table 54 shows the results of analyses of blacks from various sources of lampblack and carbon from cracking of natural gas.

In appearance carbon black is a black velvety powder with an extremely low apparent specific gravity. It owes its remarkable properties to its extreme state of division. The particles of which this powder is composed are very small, being below the resolving power of the microscope in size. Recent work on the particle size of these blacks using ultraviolet microscopic and x-ray spectrographic methods has demonstrated the impossibility of exact measurements. Discussion of the particle size of carbon blacks has been given by Goodwin and Park[63] and by the Wegelin A.-G.[64] The former employed micro-photographic methods using a milled-in mixture of black and clean pale crêpe rubber dispersed in xylene. The particle size of various blacks was found to increase in the order: Super Spectra (a channel-process black for use in varnishes), Micronex (also a channel-process black for use with rubber), Goodwin (a black made by incomplete combustion of natural gas at high temperature) and Charlton (an oil black), and Thermatomic (a black made by thermal decomposition of natural gas). The particles of Super Spectra were so fine that they could be photographed only with difficulty. Both Goodwin and Charlton blacks have particles of about equal size. Upon x-ray examination these blacks all gave the same type of pattern and breadth of line coinciding approximately with the order of particle size given above.[65] The indications are that the particles of carbon black do not exceed 0.1 to 0.2 micron (0.0001 to 0.0002 millimeter) in size, on the average, but in view of the tendency of blacks to agglomerate too much reliance cannot be placed in this figure.

Carbon black particles agglomerate when dispersed in various liquid media.[66] Under the microscope freshly prepared mixtures of thin lithographic varnish with short and long carbon blacks appear quite similar. After a few minutes, however, the particles of the short black begin to agglomerate into groups of 20 or 30 particles loosely bound together, and after an hour clusters of over a hundred have formed. These agglomerates may be resolved mechanically into their components, but they again coalesce rapidly. On the other hand, the long carbon black particles show very little tendency to agglomerate. Perrott (*loc. cit.*) suggested that the absorbed impurities (volatile matter), which are present to a larger extent in long blacks, prevent this agglomeration of particles. This conclusion is supported by the fact that treatment of long blacks with steam at

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[62] *Short flow* and *long flow* are inadequate classifications, the distinction being transitional, according to Kearsley and Roberts (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 310). A quantitative method of determining the fluidity, which is described more fully in the section on the uses of carbon black, has been proposed by them.

[63] *Ind. Eng. Chem.*, 1928, **20**, 621.

[64] *Kautschuk*, 1927, 196; *Chem. Abs.*, 1928, **22**, 184.

[65] *Cf.* Pickles, *Trans. Inst. Rubber Ind.*, 1926, **2**, 85; *Chem. Abs.*, 1926, **20**, 3838.

[66] The tendency of carbon black particles to coalesce in liquid media is modified very materially by the character of the vehicle in which the blacks are suspended. See Perrott, *U. S. Bur. Mines Bull.* **192**, 1922, 79.

TABLE 54.—*Analysis of Various Carbon Blacks, Lampblacks and Other Blacks.*[a]

Brand	Method of Manufacture	H_2O	Proximate Analysis Volatile Matter	 Fixed Carbon	Ash	H	Ultimate Analysis (Moisture-free Basis) C	 N	 O	S	Real Specific Gravity (dry basis)
		Per Cent				Per Cent					
G Elf carbon black	Large Plate	2.76	10.49	86.64	0.11	0.73	94.58	0.02	4.54	0.02	—
New Vulcan carbon black	Small Disc	3.12	5.58	91.22	0.08	0.72	96.64	0.05	2.51	0.00	1.78
Kalista carbon black	Roller	5.30	10.40	84.16	0.14	0.55	92.91	0.08	6.30	0.01	1.88
Auk carbon black..	Channel	2.64	7.06	90.30	0.00	0.59	95.04	0.06	4.31	0.00	1.85
German lampblack.	Incomplete combustion of oil	0.39	2.26	97.35	0.00	0.48	98.00	0.11	0.84	0.57	1.70
American lampblack	Incomplete combustion of oil	3.12	17.38	79.44	0.06	1.20	90.67	0.00	7.41	0.66	—
Black from cracking of natural gas	Heated retort	0.02	0.78	98.36	0.84	0.45	98.72	0.01	—	0.05	1.72
Willow charcoal ..	—	3.24	14.66	80.23	1.87	2.46	87.89	0.17	7.47	0.08	—
Bone black	—	3.88	10.92	2.68	82.52	0.47	8.99	1.10	3.53	0.06	—

[a] Perrott, *U. S. Bur. Mines Bull.* 192, 1922.

500° C. produces blacks which exhibit this tendency to agglomerate. The dispersibility of gas black has also been studied by Allen and Schoenfeld.[66a]

Because of their very fine state of division, carbon blacks always occlude large amounts of gases, mainly oxygen, nitrogen and oxides of carbon. At ordinary temperatures the composition of the gas pumped off from samples of carbon black is practically that of air, the volume of the gas being approximately equal to the volume of the voids and capillaries in the carbon. Hulett and Cude[67] obtained the results in Table 55 on pumping away the gases from various types of carbon blacks at ordinary temperatures by a Töpler pump:

TABLE 55.—*Gas from Carbon Blacks at Room Temperature.*

Material	Wt. of Black Grams[a]	Vol. of Gas Cc.[b]	—Analysis of Gas, Per Cent by Volume—					
			CO_2	O_2	CO	CH_4	H_2	N_2
Short black 1	3.2841	15.40	0.7	20.2	0.0	0.2	0.0	78.9
Short black 2	2.4206	15.25	1.4	19.1	0.2	0.1	0.0	79.2
Long black 1	3.1805	13.55	1.3	18.6	0.1	0.2	0.0	79.8
Long black 2	2.8370	16.75	0.8	22.1	0.2	0.0	0.0	76.9

[a] Free from gas and moisture.
[b] Corrected to 0° C. and 760 mm.

At higher temperatures, and particularly at 445° C., a much larger volume of gas is usually evolved, consisting chiefly of oxides of carbon. The composition and volume of gas pumped away at 445° C. are given in Table 56.

TABLE 56.—*Gas from Carbon Blacks at 445° C.*

Material	Wt. of Black Grams[a]	Vol. of Gas Cc.[b]	—Analysis of Gas, Per Cent by Volume—					
			CO_2	O_2	CO	CH_4	H_2	N_2
Short black 1	3.2841	23.02	67.2	0.9	26.2	0.0	0.0	5.7
Short black 2	2.4206	9.95	51.9	2.7	30.0	1.2	0.5	13.7
Long black 1	3.1805	25.80	64.2	0.6	12.2	0.4	0.1	22.5
Long black 2	2.8370	19.45	73.5	1.2	15.9	0.5	0.2	8.7

[a] Free from gas and moisture.
[b] Corrected to 0° C. and 760 mm.

The oxygen evolved as oxides of carbon and also as free oxygen would account for only a portion of the total oxygen present, the rest probably being held in non-volatile compounds.[68]

The rates of evolution of gas from carbon blacks at various temperatures and pressures have been recorded by Johnson.[69]

The crystalline structure of carbon black particles has been investigated by a number of workers.[70] While the consensus of opinion is that both carbon black and charcoal are essentially graphitic in nature, the evidence is not altogether convincing and authorities are not in complete agreement.

[66a] *Ind. Eng. Chem.*, 1933, **25**, 994, 1102.

[67] Reported by Perrott, *U. S. Bur. Mines Bull.* **192**, 1922. Apparatus and method are described in *J.A.C.S.*, 1920, **42**, 391.

[68] See previously recorded ultimate analyses of carbon blacks.

[69] *Ind. Eng. Chem.*, 1928, **20**, 904.

[70] See Debye and Scherrer, *Phys. Z.*, 1918, **18**, 291. See also *Engineering*, 1917, **104**, 594; *Chem. Abs.*, 1918, **12**, 449. Asahara, *Japan. J. Chem.*, 1922, **1**, 35; *Chem. Abs.*, 1923, **17**, 656. Howard and Hulett, *J. Phys. Chem.*, 1924, **28**, 1082; *Chem. Abs.*, 1925, **19**, 196. Ruff, Schmidt and Olbrick, *Z. anorg. allegem. Chem.*, 1925, **148**, 313; *Chem. Abs.*, 1926, **20**, 852. Clark, *Ind. Eng. Chem.*, 1926, **18**, 1131. Lamb, Wilson and Chaney, *Ind. Eng. Chem.*, 1919, **11**, 420. Roth and Doepke, *Ber.*, 1927, **60**, 530. Chaney, Ray, and St. Johns, *Ind. Eng. Chem.*, 1923, **15**, 1244. Oswald (*Chimie et Industrie*, 1930, **24**, 280; *Brit. Chem. Abs.* **B**, 1930, 974) has identified two varieties of amorphous carbon—a brown, truly amorphous carbon and a gray pseudo-amorphous graphitic form.

Hofmann and Groll[71] obtained a carbon having the crystalline structure of graphite by dropping benzine (boiling point 60° to 70° C.) from a capillary through a vertical quartz tube heated to 950° C. According to Plummer,[72] the theory that appears to be in greatest accord with the general properties of the so-called amorphous carbons is that they are not modifications of elemental carbon (plus certain adsorbed impurities) but that they consist of unsaturated hydrocarbons of very high molecular weight and highly deficient in hydrogen; i.e., carbon complexes in which the fields of force between the carbon atoms are unbalanced by an occasional stray hydrogen atom, thus preventing crystallization (graphitization) and producing a general state of unsaturation and hence high surface activity. This general view has also been supported by Lowry,[73] who found that the hydrogen content of charcoals heated to about 1000° C. was still 0.48 per cent and at 1300° C., about 0.1 per cent, while the coefficients of surface activity (i.e., cc. of CO_2 adsorbed per cu. mm. total pore volume) did not decrease appreciably until above 1000° C.

Of the physical characteristics of carbon blacks, adsorptive capacity is of great importance, especially as a factor in its use in rubber compositions. According to Goodwin and Park[74] this property is the one which exerts the most profound influence upon the character of a rubber mix, an influence which is more particularly shown by a tendency to retard the rate of cure of the mix and by a surface-tension effect between the pigment and the medium. This view is supported by the later work of Carson and Sebrell[75] and Wiegand and Snyder.[76] Twiss and Murphy[77] thought the differences in the rate of cure of various rubber mixes containing carbon black were attributable to the adsorption of more or less of the natural accelerator of the rubber by the filler. Other workers, however, have been unable to find any correlation between adsorptive capacity of the black and its properties in rubber mixes. Spear and Moore,[78] for example, observed no general relationship between stiffening effect or rate of cure of carbon blacks in rubber and the adsorption of either acidic or basic dyes from water or benzene. Beaver and Keller[79] also failed to note any correlation between acetone extract, iodine adsorption, or oil adsorption of carbon blacks and the rate of cure or aging of the resulting rubber compositions. They did find, however, that oxygen adsorbed on the black had a retarding effect in the mix.

The adsorptive capacity of carbon blacks has been measured by using solutions of substances such as benzoic acid,[80] iodine,[81] dyes[82] (e.g., methylene blue), oils,[83] hexamethylenetetramine,[84] alkalies,[85] diphenylguanidine,[86] and acetic acid.[87]

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[71] *Ber.*, 1932, **65B**, 1257.

[72] *Ind. Eng. Chem.*, 1930, **22**, 630. *Cf.* Bancroft, *J. Phys. Chem.*, 1920, **24**, 127.

[73] *J. Phys. Chem.*, 1930, **34**, 63; *J.A.C.S.*, 1924, **46**, 824.

[74] *Ind. Eng. Chem.*, 1928, **20**, 706.

[75] *Ind. Eng. Chem.*, 1929, **21**, 911.

[76] *Ind. Eng. Chem.*, 1931, **23**, 646.

[77] *J.S.C.I.*, 1926, **45**, 121T.

[78] *Ind. Eng. Chem.*, 1926, **18**, 418.

[79] *Ind. Eng. Chem.*, 1928, **20**, 817.

[80] Bartell and Miller, *J.A.C.S.*, 1923, **45**, 1106; Carson and Sebrell, *Ind. Eng. Chem.*, 1929, **21**, 911.

[81] Davis, *J.C.S.*, 1907, **91**, 1666; Goodwin and Park, *Ind. Eng. Chem.*, 1928, **20**, 621, 706; Johnson, *Ind. Eng. Chem.*, 1929, **21**, 1288; Carson and Sebrell, *loc. cit.*

[82] Spear and Moore, *Ind. Eng. Chem.*, 1926, **18**, 418; Ditmar and Preusse, *Gummi-Ztg.*, 1930, **45**, 243; *Chem. Abs.*, 1931, **25**, 842; *Brit. Chem. Abs.* **B**, 1931, 35; Goodwin and Park, *loc. cit.*

[83] Goodwin and Park, *loc. cit.*

[84] Spear and Moore, *loc. cit.*

[85] Wiegand, *Can. Chem. Met.*, 1929, **13**, 269; *Chem. Abs.*, 1930, **24**, 524.

[86] Wiegand, *loc. cit.*; Johnson, *loc. cit.*; Ishiguro, *J. Rubber Soc. Japan*, 1931, **3**, 11; *Chem. Abs.*, 1932, **26**, 893.

[87] Fromandi, *Kautschuk*, 1930, **6**, 27; *Chem. Abs.*, 1930, **24**, 3395; *Rubber Chemistry and Technology*, 1930, **3**, 229.

For example, Carson and Sebrell,[88] in carrying out the determination with iodine, shook 0.25 gram of the black with 50 cc. of standard iodine-potassium iodide solution and then, after centrifuging to settle the black, determined the excess iodine with standard sodium thiosulphate solution. Goodwin and Park[89] used a solution of iodine in carbon tetrachloride and allowed the black to settle by standing, with, if necessary, the addition of diatomaceous earth.

Wiegand and Snyder[90] determined the adsorptive capacity of carbon black by using diphenylguanidine. One gram of the black is shaken for 2 hours with 50 cc. of an alcoholic solution of diphenylguanidine (2 grams per liter of alcohol), the black is removed by filtration, and the quantity of diphenylguanidine remaining is determined by titration of 25 cc. of the filtered alcohol with standard hydrochloric acid, using a mixture of bromophenol blue and methyl red as the indicator.

Very intimately connected with the subject of adsorptive capacity is that of the adhesion tension of blacks. This subject has been discussed by Bartell and Smith,[91] who measured the adhesive values of several commercial blacks against water and benzene. The method of Bartell and Osterhof,[92] which they used, depends upon the measurement of the pressure set up when a given liquid displaces air, or a second liquid, from a membrane of finely divided solid material packed in a displacement cell. It was shown that different commercial blacks possess different adhesive tensions against water and benzene and that heat treatment of the blacks tends to reduce this tension. According to Bartell and Miller[93] a direct relationship exists between adhesive tension and adsorption when a given solid is used with different liquids.

The heats of combustion of carbon blacks and various other forms of elemental carbon have been determined by Roth and Doepke[94] and Plummer.[95] Perhaps the most remarkable result of the work of the latter is the observation that the heats of combustion of carbon blacks which have been degassed at 1000° C. are higher than that of graphite and, in fact, are the highest of any known form of carbon. Roth and Doepke and Plummer found that prolonged heating at 1000° C., or higher, results in a gradual lowering of the heat of combustion, a result which is to be ascribed to slow crystallization (graphitization). Plummer's results for various carbons subjected to different treatments are given in Table 57.

TABLE 57.—*Heats of Combustion of Carbon Blacks.*

Sample	Oven Dried at 110° C.	Degassed at 1000° C.	
		Weighed in Air	Weighed *in vacuo* [a]
	cal./gm.		
Standard channel carbon black	7812	8181	8272
Compressed channel carbon black	7939	8221	—
Acheson graphite No. 2301	7875	—	7932

[a] Corrected to weight-in-air basis.

The value of 8272 calories per gram for degassed and vacuum-weighed channel carbon black is the highest value observed for any form of carbon, being

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[88] *Loc. cit.*

[89] *Loc. cit.*

[90] *Ind. Eng. Chem.*, 1931, **23**, 646.

[91] *Ind. Eng. Chem.*, 1929, 21, 1102. See also Bartell and Osterhof, "Colloid Symposium Monograph," Chemical Catalog Co., Inc., New York, 1927, 5, 113.

[92] *Loc. cit.*

[93] Unpublished work reported by Bartell and Smith. See Bartell and Sloan, *J.A.C.S.*, 1929, **51**, 1637, 1643; Bartell and Greager, *Ind. Eng. Chem.*, 1929, 21, 1248; Bartell and Miller, *Ind. Eng. Chem.*, 1932, **24**, 335.

[94] *Ber.*, 1927, **60**, 530.

[95] *Ind. Eng. Chem.*, 1930, **22**, 630.

340 calories per gram higher than that obtained for graphite. Roth and Doepke found a difference of 292 calories per gram between graphite and their "most highly" amorphous carbon and attributed this difference to the existence of a distinct modification of amorphous carbon. A somewhat different interpretation, involving the existence of highly unsaturated high molecular weight hydrocarbons, substantiated by this work, has been previously discussed.

The color and tinting power of carbon blacks has been correlated with their other physical properties by Perrott,[96] Johnson[97] and Hock.[98] Goodwin and Park[99] determined the tinting strength of various blacks by mixing 0.05 gm. of the black with a known weight of zinc oxide in boiled linseed oil until a standard color intensity (Micronex carbon black with 2 grams zinc oxide) was attained. Their results, which are given in Table 58, were considered to indicate the particle size, except possibly in the case of Super Spectra, which was probably so finely divided as to have passed the optimum obscuring power.

TABLE 58.—*Tinting Strength of Various Blacks.*

Carbon Black	Oil Used Drops	Zinc Oxide Grams	Relative Tinting Strength
Charlton	60	1.275	0.63
Micronex	60	2.000	1.00
Super Spectra	60	1.778	0.88
Thermatomic	20	0.263	0.13
Goodwin	40	0.996	0.50

In this discussion the properties of only a few carbon blacks have been tabulated. Comparisons have also been reported for other varieties, using the methods and procedures already outlined. Thus, Dawson and Hartshorne[100] analyzed acetylene black and lampblack. The properties of the Thermatomic[101] carbon blacks, Thermax and P-33, have been evaluated and Plummer[102] has reported the characteristics of carbon blacks made from propane.

The properties of a carbon black called "Gastex," made by the partial combustion of natural gas, have also been reported.[103] Table 59 gives a comparison of the properties of "Gastex" with those of other carbon blacks:

TABLE 59.—*Comparison of Properties of "Gastex" and Other Carbon Blacks.*

Black	Oil Adsorption Cc./100 Gm.	Iodine Adsorption Gm./1000 Gm.	Moisture	Acetone Extract	Ash	Specific Gravity	Color Value
			Per Cent				
Ink	146	79.0	6.0	0.36	0.02	1.88	100
Channel	140	57.0	2.5	0.20	0.10	1.73	100
"Gastex"	100	22.0	0.5	0.50	0.08	1.82	50
Acetylene	296–350	43.0	0.2	0.36	0.05	1.84	50
Thermatomic	46	6.1	0.1	0.47	0.30	1.84	13
Lampblack	130	9.2	3.0	0.84	0.10	1.73	20

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[96] *U. S. Bur. Mines Bull.* 192, 1922.
[97] *India Rubber World*, 1927, 77, No. 5, 65; *Chem. Abs.*, 1928, 22, 1252.
[98] *Kautschuk*, 1928, 4, 266; *Chem. Abs.*, 1929, 23, 1772.
[99] *Ind. Eng. Chem.*, 1928, 20, 621.
[100] *Trans. Inst. Rubber Ind.*, 1930, 5, 48; *Brit. Chem. Abs.* B, 1931, 6.
[101] Moore, *Ind. Eng. Chem.*, 1932, 24, 21.
[102] *Ind. Eng. Chem.*, 1930, 22, 1209.
[103] Anon., *Oil and Gas J.*, 1928, Dec. 6, 237.

USES OF CARBON BLACK

The carbon black industry is dependent on the availability of large supplies of cheap natural gas and cannot survive in localities where higher-priced uses for the gas have been found. This fact explains why the industry has had to migrate from West Virginia into Louisiana (about 1920) and later (1928) into the Panhandle (Texas) district. Until the utilization of gas from the prolific fields of Louisiana, about 75 per cent of the world's supply of black was manufactured in West Virginia.[104] In 1929 the industry was largely located in Texas and Louisiana, while less than 3 per cent of the total output of carbon black represented the combined production of West Virginia, Wyoming, Oklahoma, Montana, and Kentucky.[105]

Of the natural gas used in 1929, about 14 per cent of the total was consumed in the manufacture of carbon black. About 87 per cent of the gas which was burned for carbon black was stripped for gasoline. The carbon black industry and the natural-gas gasoline industry are obviously complementary to some extent.[106]

Carbon black is used extensively in the manufacture of the following products, the percentages indicating the proportion of the total domestic deliveries in 1931: (1) rubber (83%), (2) ink (9%), (3) pigments and enamels (4%), and (4) other products (4%), such as shoe and stove polishes, gramophone records, carbon papers, typewriter ribbons, bookbinder's board, hard rubber, artificial stone, crayons and insulating materials. The statistics in Table 60 indicate the total production of carbon black in the United States in 1928, 1929, 1930 and 1931, and the distribution in its various applications.

TABLE 60.—*Production of Carbon Black in the United States.*

Production (in pounds)	1928	1929	1930	1931
By Channel process	220,532,000	327,552,000	350,254,000	255,322,000
By other processes (including disc, Lewis, roller, "special" and Thermatomic)	28,258,000	38,890,000	29,688,000	25,585,000
Total pounds	248,790,000	366,442,000	379,942,000	280,907,000
Domestic Sales (in pounds)				
To rubber companies	140,938,000	138,474,000	128,572,000	134,315,000
To ink companies	27,223,000	27,350,000	19,220,000	15,184,000
To paint companies	20,040,000	17,257,000	11,922,000	6,760,000
For miscellaneous purposes	14,475,000	8,896,000	7,565,000	5,453,000
Exported	77,903,000	91,829,000	84,260,000	96,714,000
Total pounds	280,579,000	283,806,000	251,539,000	258,426,000

Carbon black, which was first added to rubber as a pigment about 1915, has almost completely displaced zinc oxide as a filler in the rubber industry. It is used in all kinds of rubber materials but its use in tires is by far the most important application.[107] Carbon black is used in automobile tread stocks in quantities up to 45 per cent of the rubber or 27 to 28 per cent of the final composition. As illustrating the effect and importance of carbon black in such a use it may be stated that 2 pounds of black suitably incorporated in a small tire will increase the life of the tire from 5,000 miles to about 20,000 miles. The increased durability of tires containing carbon black has saved motorists millions of dollars. From a theoretical viewpoint, carbon black is an ideal filler because of its finely divided condition and low specific gravity. It appears to protect the rubber substance from the effects of light and may retard oxidation.[108]

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[104] Neal, *U. S. Bur. Mines Bull.* **192**, 1922.

[105] Hopkins and Backus, *Mineral Resources of the United States*, 1929, **2**, 51-59; see also reports for 1931 (*Chem. Met. Eng.*, 1932, **39**, 380).

[106] Hopkins and Backus, *loc. cit.* See also Carney, *J. Inst. Pet. Tech.*, 1930, **16**, 118; *Chem. Abs.*, 1930, **24**, 5134.

[107] The use of carbon black in rubber insulating compounds has been discussed by Wiegand and Boggs (*Ind. Eng. Chem.*, 1930, **22**, 822). Mixtures of rubber, carbon black, and a tasteless mineral oil have been suggested as substitutes for chicle in chewing gum (Zimmerli and Semon, U. S. Patent 1,829,029, Oct. 27, 1931; assigned to B. F. Goodrich Co.). For effects of carbon in rubber see also Spear and Moore, *Ind. Eng. Chem.*, 1926, **18**, 418.

Lampblack has been used since the invention of the printing press as a pigment in printer's ink but since 1864 it has been almost entirely replaced by carbon black. The latter is now absolutely indispensable in the manufacture of most inks, the various blacks being carefully chosen for the purpose according to their particular characteristics. As pointed out previously, certain blacks produce the so-called short inks (i.e., inks of buttery consistency which do not flow rapidly), which are especially suitable for lithographic and offset work, in slow-speed presses and for most half-tones. For these purposes lampblack is unsuitable. Other types of black produce the so-called long inks which, on account of their more rapid flow and opacity, are employed in fast-running presses. Attention should be directed to the fact, however, that the largest application of carbon blacks in ink involving the highest speed presses, namely news ink, actually makes use of short channel blacks. This is because news inks are not made with a varnish base as are book inks, but are manufactured with ordinary non-drying and free-flowing petroleum oils.

Kearsley and Roberts [109] have suggested a method for determining the effect of carbon black on the fluidity of printing ink. Their procedure consists in mixing carbon black with ten times its weight of a standard lithographic varnish, and allowing ten drops of the mixture to drop onto a horizontal glass plate maintained at a definite temperature. After allowing the mixture to come to the temperature of the plate the latter is then set at an angle of 30° and the rate of flow of the carbon black mixture is determined.

Carbon black is finding increasing application as a pigment in various paints and enamels. It has a higher tinting strength than any other black and is generally acknowledged to be superior for varnishes and enamels. The application of carbon black as a coloring agent in paints, varnishes, and lacquers accounted for deliveries of 17,257,000 pounds in 1929, or 9 per cent of the total domestic sales.[110] Both long and short carbon blacks ordinarily possess a reddish-brown undertone which can be partially corrected by the use of blue dyes ("toners") but which renders these blacks unsatisfactory for certain inks. In certain gray tints, however, lampblack may be superior to carbon black on account of its bluish-gray tone.

For other purposes, carbon black is employed because of its high coloring power, highly dispersed condition, and low cost. Although it may be possible to substitute lampblack for carbon black for some purposes (for example, in the manufacture of phonograph records, medical hard rubber, and certain types of inks and paints), the question of such substitution is largely a matter of economics. The relative development of the natural-gas industry in the United States and of the coal-tar industry in Europe create an economic urge toward the use of carbon black in the United States and of lampblack in Europe, whenever possible.[111]

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[108] Perrott, *loc. cit.*

[109] *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 310.

[110] This dropped to 6,760,000 pounds in 1931 or 4 per cent of the total domestic sales.

[111] A discussion of the manufacturing difficulties encountered by the German carbon black industry is given by Hadert, *Paint and Varnish Production Mgr.*, 1932, 7, No. 5, 32; *Chem. Abs.*, 1932, 26, 3336.

TESTING OF CARBON BLACKS

Neal and Perrott,[112] in their account of the carbon black industry, described a number of physical and chemical tests which may be used for determining the characteristics of a sample of carbon black and its probable value for various purposes. Some of these tests and results have already been discussed in a previous section of this chapter. Of the chemical tests the determinations of moisture and ash are most useful.

The moisture content, which is determined by heating a sample of black for 1 hour at 105° C. in a constant-temperature oven in circulating dry air, should not be more than 4 or 5 per cent for use in printing inks or rubber. Table 61 gives the figures found by Goodwin and Park[113] for the moisture content of various typical blacks, in per cent of the original weight. After the moisture content was determined the dried blacks were placed in an ice box for 24 hours. The gain in weight is given in the second column as per cent (on the basis of the dry sample) fluctuation of moisture.

TABLE 61.—*Moisture Content of Blacks.*

Black	Moisture	Fluctuation of Moisture
	——Per Cent——	
Charlton	2.90	3.5
Micronex	2.80	3.8
Super Spectra	5.70	6.7
Thermatomic	0.06	0.3
Goodwin	0.08	0.5

The differences in moisture content appear to depend upon the adsorptive capacity of the black.

The ash content, determined by ignition to about 750° C. (a cherry-red heat), should not exceed about 0.2 per cent for most purposes. Higher results indicate adulteration with mineral black or charcoal.

The determination of the organic material extractable by boiling acetone has been shown by Goodwin and Park[114] to be a matter of some difficulty owing to the tenacity with which the material is retained by the black. The fact that extracted material is readsorbed when placed in contact with the original material is further evidence that the extraction process involves an adsorption equilibrium. The method of extraction preferred by them consists in extracting 1 to 2 grams of the air-dried black together with 3 or 4 grams of diatomaceous earth with boiling acetone for 5 days in an Underwriter's apparatus. The extract is then dried overnight at 56° C. and weighed. The extraction of the five blacks investigated gave the results shown in Table 62.

TABLE 62.—*Acetone Extraction of Blacks.*

Black	Extract Per Cent
Charlton	3.70
Micronex	0.23
Super Spectra	0.27
Thermatomic	1.64
Goodwin	1.44

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[112] *U. S. Bur. Mines. Bull.* **192**, 1922.
[113] *Ind. Eng. Chem.*, 1928, **20**, 621.
[114] *Loc. cit.*

In the opinion of Goodwin and Park, the amount of extractable matter bears no relation to the quality of the black, and since it is practically impossible to determine the total extractable matter, they attach little importance to this test.

Other useful characteristics are the real and apparent densities of the sample. Details of the methods for this determination are also given by Goodwin and Park and they report the values for typical blacks shown in Table 63.

TABLE 63.—*Specific Gravities and Apparent Densities of Blacks.*

Black	True Specific Gravity	Apparent Density, Gm./cc.
Charlton	1.66	0.15
Charlton (extracted with acetone)	1.71	—
Micronex	1.79	0.26
Super Spectra	1.89	0.11
Thermatomic	1.84	0.65
Goodwin	1.82	0.12

The other tests, such as the estimation of tinting power, color, grit, and hiding power or spreading rate, are empirical but are valuable in deciding the possible application of the black.

Butcher[115] and Cranor and Venuto[116] have also outlined methods of testing carbon black.

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[115] *Chem. Trade J.*, 1930, 87, 399; *Chem. Abs.*, 1931, 25, 383.

[116] *Am. Paint J.*, 1931, 15, No. 26, 21.

Chapter 9

Transformation of Hydrocarbons by Electrical and Other Special Forms of Energy

Electric treatment of hydrocarbons may be roughly classified according to whether the energy is supplied by an electric arc (sparking), or by a silent electric discharge, often called *voltolization.* Treatment with alpha particles and similar forms of energy could be included in the latter category. Although in many cases a similar ultimate result may be attained by either method, yet there are important differences. Chemically, the major difference is that the electric arc involves cracking of the molecule into smaller fragments or radicals, whereas the silent electric discharge generally induces polymerization into larger molecules, often accompanied by dehydrogenation. In the silent electrical discharge a relatively thin film of material is subjected to a high voltage between highly charged surfaces, but no actual sparking takes place. In the high-tension arc, sparking occurs across a permanent gap and in the low-tension arc, the electrode is first raised to a high temperature heating the surrounding gas so that it becomes a good conductor and allows the passage of a current in the form of an arc at comparatively low voltages.

THE ELECTRIC ARC

The action of the electric arc, or of electric sparks, on various types of hydrocarbons produces extensive decomposition accompanied by the formation of numerous products of which carbon, hydrogen and acetylene are usually important. Because of the intense heating effect of the arc, its action is, in many respects, comparable to the changes taking place when hydrocarbons are subjected to severe pyrolytic operations.[1]

Of the early investigators, Dalton[2] and Henry[3] reported that methane was decomposed into carbon and hydrogen by electric sparks.[4] When "pit gas," freed from carbon dioxide, was subjected to such treatment for 30 hours, Bischof[5] observed that only one-third of the methane had decomposed and the carbon formed possessed a strong odor of turpentine. He therefore attributed the complete decomposition observed by Dalton to the presence of moisture in the gas. Buff and Hofmann,[6] Franchimont,[7] Lepsius[8] and Plesniewicz[9] have also resolved methane into carbon and hydrogen by treatment with electrical sparks.

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[1] Lefebvre and Montagne, *Bull. soc. encour. ind. nat.*, 1928, 917; *Chem. Abs.*, 1929, **23**, 2368.

[2] "System of Chemistry," Manchester, 1808, **2**, 255.

[3] *Phil. Trans.*, 1809, **99**, 430; *ibid.*, 1821, 111, 136.

[4] See also Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1852, 7, 253.

[5] *Edinburgh New Phil. J.*, 1840, **28**, 183; *ibid.*, 1840, **29**, 309.

[6] *Ann.*, 1860, **113**, 129.

[7] *Rec. trav. chim.*, 1882, 1, 275; *Chem. Zentr.*, 1883, 1, 209.

[8] *Ber.*, 1890, **23**, 1642.

[9] *Rocz. Chem.*, 1926, **6**, 741; *Chem. Abs.*, 1927, **21**, 3290.

This action of the electric arc on mixtures of hydrocarbon gases is the basis of a number of processes for making hydrogen.[10]

Berthelot[11] was probably the first to show that considerable quantities of acetylene were produced when methane, and other hydrocarbons, were subjected to the electric arc. Ludeking[12] pointed out that methane yields hydrogen and carbon when both the electrodes are metallic or one is metallic and the other carbon, but that acetylene is formed when both electrodes are made of carbon.

The formation of acetylene from other hydrocarbons by the action of an electric arc, either high or low tension, is of practical importance and is associated from a scientific point of view with the increasing thermodynamic stability of that substance at high temperatures.

Bone and Jerdan[13] showed that the direct combination of carbon and hydrogen to yield acetylene could take place in the electric arc, so that the reaction

$$C_2H_2 \rightleftharpoons 2C + H_2$$

was reversible under such conditions. These same investigators, by the prolonged action of an electric arc on methane, admixed with a small quantity of nitrogen, obtained a gas having the composition, hydrogen cyanide 0.8 per cent, hydrogen 85.6 per cent, acetylene 9.8 per cent, methane 2.5 per cent and nitrogen 1.3 per cent. Of interest in this connection is the production of saturated hydrocarbons, which Carter and Campbell[14] stated takes place under the influence of a low-voltage carbon arc discharge in water. At the same time a small proportion of a sparingly soluble acid of high melting point is obtained.

The effect of a high-tension arc on substantially pure methane has been investigated by Stanley and Nash.[15] The main products of the reaction were acetylene, carbon and liquid and solid hydrocarbons, though ethylene and a small proportion of diacetylene ($HC{\equiv}CC{\equiv}CH$) were also found in the reaction gas. In addition to gaseous products and carbon, small quantities of light oil, chloroform-soluble tar, and resinous substances were produced. The light oil was highly unsaturated, had a pronounced tendency to resinify, and formed explosive silver derivatives, thus indicating that acetylene homologues were present. Both naphthalene and acenaphthylene were isolated from the tar. The occurrence of diacetylene among the reaction products is interesting since this hydrocarbon has been obtained in other operations, particularly in the electropyrolysis of alcohol[16] and the treatment of fuel oil with a low-tension arc.[17]

Frolich, White, Uhrmacher and Tufts[18] recorded some experiments on the decomposition of methane in an ordinary carbon arc. Acetylene was the main product under all conditions, although some ethylene (up to 1.5 per cent in the resulting gas) was formed also. Carbon deposition was largely suppressed and the acetylene yield markedly increased by diluting the methane with hydrogen. With methane and hydrogen in the ratio of 1:2 as much as 51 per cent of the methane was converted into acetylene by one passage through the arc. It was suggested by Frolich and his collaborators that the added hydrogen reduces carbon deposition because of its influence on the high-temperature equilibrium.

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[10] See for example, I. G. Farbenindustrie A.-G., British Patent 263,859, 1925; *Chem. Abs.*, 1928, **22**, 32; British Patent 307,529, 1927; *Chem. Abs.*, 1929, **23**, 5282. Wietzel, Stark and Eisenhut, German Patent 488,502, 1926; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 2251. Rose, U. S. Patents 1,352,085 and 1,352,086, Sept. 7, 1920; *J.S.C.I.*, 1920, **39**, 715A.

[11] *Ann.*, 1862, **123**, 213. "Essai de méchanique chimique," 1879, **2**, 336. *Ann. chim. phys.*, 1873, (4) **30**, 431; *J.C.S.*, 1874, **27**, 974.

[12] *Phil. Mag.*, 1892, (5) **33**, 525.

[13] *J.C.S.*, 1897, **71**, 41; 1901, **79**, 1042.

[14] *Trans. Faraday Soc.*, 1932, **28**, 479; *Chem. Abs.*, 1932, **26**, 3734.

[15] *J.S.C.I.*, 1929, **48**, 238T.

[16] Müller, *Helv. Chim. Acta*, 1925, **8**, 821; *Chem. Abs.*, 1926, **20**, 1050. Dutt (French Patent 677,338, 1928; *Chem. Abs.*, 1930, **24**, 2956) obtained ethylacetylene by the electrolytic disaggregation of calcium carbide electrodes in methyl alcohol.

[17] Curme, U. S. Patent 1,315,540, Sept. 9, 1919; assigned to Union Carbide Co.; *Chem. Abs.*, 1919, **13**, 2817.

[18] *Ind. Eng. Chem.*, 1930, **22**, 23.

$$C_2H_2 \rightleftharpoons 2C + H_2$$

since this reaction has been shown to be reversible under the experimental conditions. When ethane was passed through the arc, acetylene and ethylene were obtained in approximately equal volumes, while, as in the case of methane, low gas velocities resulted chiefly in the cracking of the hydrocarbons to carbon and hydrogen.

When employing voltages ranging from 8,000 to 47,000, methane, ethane, and ethylene are transformed to acetylene and hydrogen, together with other substances.[19] In the case of methane, acetylene and hydrogen, in the ratio of 1 : 5, were formed; ethane yielded a variety of materials including hydrogen, acetylene, methane and ethylene; and ethylene gave hydrogen and acetylene, in the ratio of about 2:1, and some methane. Heptane vapors at 4 to 12 mm. pressure, however, when subjected to a low-tension discharge (300 to 600 volts between nickel electrodes) yielded hydrogen and a condensation product.[20] The latter had practically no vapor pressure, was slightly soluble in organic solvents, and slowly absorbed oxygen from the air.

A study of the decomposition of liquid and solid hydrocarbons in the (low tension) electric arc was made by Contardi.[21] This was an endeavor to obtain an insight into the mechanism of cracking, and various hydrocarbons such as benzene, hexane, amylene, toluene, pseudocumene, petrolatum, paraffin, naphthalene, and others were subjected to an explosive electrical discharge under different conditions. Hydrocarbons of widely different types yielded gaseous products of a similar character indicating that the chief reactions were the same in all cases. The analytical data showed that the first two of these, namely,

$$\begin{array}{ll} & 2CH_4 \longrightarrow C_2H_2 + 3H_2 \\ \text{and} & C_2H_6 \longrightarrow C_2H_2 + 2H_2 \end{array}$$

proceeded with enormous velocities in the hot zone. The secondary reactions. viz.,

$$\begin{array}{ll} & C_2H_2 \longrightarrow 2C + H_2 \\ & C + 2H_2 \longrightarrow CH_4 \\ \text{and} & 2C + 3H_2 \longrightarrow C_2H_6 \end{array}$$

which occur at the same time, are completed in the cold zone (1200° C.) at the expense of the carbon formed. Methane and ethane, on account of the latter reactions, do not again reach the hot zone and so appear in the final products. Hydrocarbons very rich in hydrogen, e.g., hexane, yielded a gas which at first contained about 18 per cent of acetylene. On continued action of the electrical discharge the liquid became heavily charged with carbon and the acetylene content of the gas increased to 33-34 per cent.

In some experiments on the production of acetylene in the electric arc by methods applicable on an industrial scale, Contardi directed his attention to the use of coal tar and anthracene oil. In an arc between iron or carbon electrodes at 50 volts and 40 amperes, anthracene oil yielded a gas containing 22 per cent acetylene, 50 per cent methane, 23 per cent hydrogen and 5 per cent nitrogen. Graphitic carbon was deposited at the same time. The temperature of the oil in which the electrodes were immersed did not exceed 120° to 130° C. A coal-tar oil gave a gas having the composition 24 per cent acetylene, 45.4 per cent methane and 0.8 per cent nitrogen. Carbon deposition amounted to about 10 per cent of the oil.

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[19] Fujio, *Bull. Chem. Soc. Japan*, 1930, 5, 249; *Chem. Abs.*, 1930, **24**, 5644.

[20] Christen, *Anales inst. investigaciones cient. tecnol.*, 1932, 1, 71; *Chem. Abs.*, 1933, **27**, 4743.

[21] *Atti congresso naz. chim. ind.*, 1924, 358; *Chem. Abs.*, 1925, **19**, 1941. *Giorn. chim. ind.*, 1925, 7, 195; *Chem. Abs.*, 1926, **20**, 3230.

Attention has been given to the possibility of making acetylene by the action of the electric arc on mixtures of saturated gaseous hydrocarbons, such as natural gas, coal gas or coke-oven gas, which contain a large proportion of methane. The results of such an investigation have been reported by Fischer and Peters.[22] The main portion of their work was concerned with the action of high-tension sparks on coke-oven gas containing principally methane and hydrogen (23.4 per cent methane and 52.3 per cent hydrogen) at pressures of 2 to 60 mm. At reduced pressures the number of ions is enormously increased, a fact which leads to the supposition that under such conditions the efficiency of the discharge would be greatly enhanced. A reaction chamber of glass having iron electrodes 20 to 120 mm. apart was used. The main gaseous products of the reaction were observed to be acetylene and hydrogen, together with some ethane. The best conditions for obtaining acetylene were a pressure of 40 to 50 mm., a distance between electrodes of 40 mm., and high gas rates. Under such conditions the reaction gas contained 8.5 per cent of acetylene and the energy consumed per cubic meter was 31 kilowatt-hours, with an efficiency of 15 per cent. Experiments with pure methane were rendered difficult owing to the formation of carbon in the reaction chamber.

Further work on the conversion of methane in coke-oven gas into acetylene under reduced pressures has been recorded by Peters and Pranschke.[23] They were able to reduce the energy required from 31 to 12 kilowatt-hours per cubic meter of acetylene, thereby increasing the electrical efficiency from 15 to 38 per cent. They also found that best results were obtained with gas mixtures containing 50 per cent or less of methane. When the methane content was higher than 50 per cent the acetylene formed apparently took part in other reactions.

Peters and Wagner[24] determined the minimum energy consumption for the production of acetylene or ethylene to be 13 and 53 kilowatt hours per cubic meter, respectively. Under these conditions using a gas mixture containing 2 moles of methane and 1 mole of hydrogen, the exit gases contained 4.2 per cent acetylene and 0.8 per cent ethylene. It was apparently impossible to suppress acetylene and increase ethylene production except at very low pressures and high energy consumptions. Generally the proportion of acetylene in exit gases increased with the energy supplied, the maximum concentration being 30 per cent. In the case of ethylene the maximum concentration did not exceed 3 per cent.

The effect of reducing the pressure during the electrical decomposition of natural gas (92.5 per cent methane, 3.5 per cent hydrogen, and 3.9 per cent nitrogen) was investigated by Jones.[25] Platinum wire electrodes were employed, and the pressure was varied from 100 to 700 mm. of mercury. Analysis of the gaseous products appeared to indicate that the main reaction was the decomposition of methane into carbon and hydrogen, although high percentages of olefinic and acetylenic hydrocarbons were formed. The highest yield of acetylene was obtained at about one-half an atmosphere pressure. At still lower pressures, 1 to 11 mm., Montagne[26] believed the principal reaction to be the decomposition of methane into acetylene and hydrogen (proceeding to the extent of about 75 per cent) but this is complicated by subsequent decomposition and condensation of the acetylene. Even at low temperatures (e.g., liquid air) as much as 10 per cent of the methane is transformed into saturated or ethylenic hydrocarbons.

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[22] *Brennstoff-Chem.*, 1929, **10**, 108; *Chem. Abs.*, 1929, **23**, 4326.

[23] *Brennstoff-Chem.*, 1930, **11**, 239; *Chem. Abs.*, 1931, **25**, 399.

[24] *Z. phys. Chem.*, 1931, **153**, 161; *Brit. Chem. Abs.* **A**, 1931, 441. See also Peters and Neumann, *Brennstoff-Chem.*, 1933, **14**, 165; *Chem. Abs.*, 1933, **27**, 4906.

[25] *J.C.S.*, 1929, 419.

Although acetylene is the principal hydrocarbon resulting from the action of the electric arc on hydrocarbons under most conditions, nevertheless other substances may be obtained in considerable yields. Ethylene appears to be an important product, and diacetylene, as previously noted, has been observed in some instances. Curme[27] has developed a process for decomposing fuel oil in a regulated alternating current arc into a gas consisting of about 50 per cent hydrogen, 12.5 per cent ethylene, 25 per cent acetylene and 5 per cent of other hydrocarbons among which diacetylene is an important constituent. The relatively high proportion of ethylene in comparison with the acetylene yield is noteworthy. According to Brooks,[28] Curme was able to prepare diacetylene in considerable quantities and to determine accurately the properties of this hydrocarbon.

Diacetylene was prepared by Müller and Bänninger[29] by the decomposition of benzene in a low-tension arc. Some higher acetylenes were formed at the same time, as well as phenylacetylene, $C_6H_6C{\equiv}CH$. The gaseous reaction products contained 86 to 87 per cent hydrogen and 9 to 10 per cent of acetylene. To explain these results, it was assumed that a primary dissociation of the benzene into the radicals C_6H_5— and $CH{\equiv}C$— was followed by a secondary recombination of such radicals.

Under certain conditions, moreover, it appears that higher olefins and diolefins may be produced from lower members of the olefin series (particularly ethylene) when the latter are exposed to a high-temperature arc at a higher rate of flow than that required for making acetylene.[30]

The gaseous products of the decomposition of mineral oils by a high-tension arc have been examined by Evers.[31] Some of these were found to contain as high as 50.3 per cent hydrogen and 45 per cent unsaturated hydrocarbons, and only about 1 per cent methane. The unsaturated hydrocarbons were separated as bromides, and from the less volatile fractions a bromide, $C_6H_4Br_8$, was isolated which melted at 82.8° C. In addition some liquid materials as well as a dark brown solid of variable composition (90 to 94 per cent carbon, 3 per cent hydrogen, and 4 to 7 per cent oxygen) were obtained.

Mention has been made of the effect of diluting methane with hydrogen before subjecting it to the electric arc. Other gases may be employed, the effect created varying with the individual gas used. The substitution of ammonia, for example, for hydrogen results in the formation of hydrogen cyanide, a 1:1 mixture of methane and ammonia giving a 70 per cent yield.[32] With higher proportions of ammonia, as in a 3:7 methane-ammonia mixture, a good yield of crystalline ammonium cyanide is secured. The addition of ammonia prevents the accumu-

[26] *Compt. rend.*, 1932, **194**, 1490; *Brit. Chem. Abs.* **A**, 1932, 580; *Bull. soc. d'encour.*, 1933, **132**, 183; *Brit. Chem. Abs.* **A**, 1933, 576.

[27] U. S. Patent 1,315,540, Sept. 9, 1919; assigned to Union Carbide Co.; *Chem. Abs.*, 1919, **13**, 2817.

[28] *Ind. Eng. Chem.*, 1924, **16**, 185.

[29] *Helv. Chim. Acta*, 1927, **10**, 763; *Chem. Abs.*, 1928, **22**, 395.

[30] Feiler, U. S. Patent 1,799,787, Apr. 7, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3012.

[31] *Wiss. Veröff. Siemens-Konz.*, 1925, **4**, 324; *Brit. Chem. Abs.* **B**, 1926, 308. For an account of some experiments on the cracking of mineral oils in the electric arc, see Fester and Christen, *Z. Elektrochem.*, 1930, **36**, 17; *Chem. Abs.*, 1930, **24**, 4382.

[32] Peters and Küster, *Brennstoff-Chem.*, 1931, **12**, 122; *Chem. Abs.*, 1931, **25**, 2922.

lation of hydrocarbons, since both tars and hydrocarbons react with it to form hydrogen cyanide.

When mixed with carbon dioxide, or steam, and subjected to a high voltage (5,000 to 6,000) arc, methane is converted to carbon monoxide.[33]

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$
$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

No deposition of carbon takes place. With a lower voltage a part of the methane is converted into acetylene. By varying the voltage and the initial gas mixture the composition of the reaction gas can be altered over a wide range.

Many of the industrial processes dealing with the decomposition of hydrocarbons, either liquid or gaseous, are concerned with the production of acetylene and hydrogen. Methane is especially mentioned as appropriate raw material in several of these, probably because of its abundance and cheapness. This is of particular interest in connection with the better utilization of natural gas, of which methane forms the preponderating constituent, since the resulting acetylene may be employed in welding operations or in the preparation of numerous organic substances. A survey of such processes for making acetylene and hydrogen indicates that they differ principally in constructional details of the equipment. In one procedure the gases, containing both methane and hydrogen, are passed through the arc at atmospheric pressure, the deposition of carbon being prevented by the hydrogen.[34]

Gross[35] described a method in which coal gas, containing both methane and ethylene, is subjected to an electric discharge by passage through a reaction chamber consisting of the annular space between a conical rotor and a conical stator. On both of these, projections (serving as the electrodes) are arranged spirally. The reaction gas is subsequently compressed to remove tarry constituents, and is then bubbled through an absorbent (e.g., acetone) to separate acetylene. In this manner one ton of coal gas is said to yield 280 cubic meters of acetylene.

In another form of apparatus, designed by Gmelin and Eisenhut,[36] the hydrocarbon gases or vapors are passed through an arc formed between a central insulated electrode grounded at the end and a surrounding tubular counter-electrode. The length of arc can be adjusted by a movable insulating mantle of quartz or steatite between the electrodes so as to obtain optimum production of acetylene. Mixtures of hydrogen and methane can be used as the initial materials, but the yield of actylene is materially increased by the presence of other hydrocarbons, either saturated or unsaturated (e.g., ethane, ethylene or oil gas). Thus, mixtures containing (1) 30 per cent methane and 70 per cent hydrogen, (2) 15 per cent methane and 85 per cent ethylene, and (3) 30 per cent ethylene and 70 per cent hydrogen, when conducted through the apparatus give 70 to 80 liters, 100 to 110 liters, and 110 to 140 liters, respectively, of acetylene per kilowatt-hour of electrical energy expended. In a related process[37] acetylene in the exit gas is converted to benzene, which is removed by adsorption with activated charcoal, and the residual gases are treated with oxygen or steam forming a mixture of carbon monoxide and hydrogen.

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[33] Peters and Pranschke, *Brennstoff-Chem.*, 1930, 11, 473; *Brit. Chem. Abs.* **B**, 1931, 186.

[34] Andry-Bourgeois, British Patent 223,543, 1924; assigned to Le pétrole synthétique; *J.S.C.I.*, 1925, 40, 534B.

[35] British Patent 211,125, 1924; *J.S.C.I.*, 1925, 40, 622B.

[36] U. S. Patent 1,746,934, Feb. 11, 1930; *Brit. Chem. Abs.* **B**, 1930, 314; British Patent 294,494, 1927; *Brit. Chem. Abs.* **B**, 1928, 738; French Patent 626,795, 1927; all assigned to I. G. Farbenindustrie A.-G. Structural details of apparatus for the electrolytic treatment of hydrocarbons to effect their conversion are described by I. G. Farbenindustrie A.-G., French Patent 746,595, 1933; *Chem. Abs.*, 1933, 27, 4490; Henry, U. S. Patent 1,881,406, Oct. 4, 1932; assigned to Ionizing Corp. of America; *Chem. Abs.*, 1933, 27, 592.

[37] I. G. Farbenindustrie A.-G., British Patent 269,547, 1927; *Brit. Chem. Abs.* **B**, 1928, 291. Also, Wietzel and Starke, U. S. Patent 1,892,973, Jan. 3, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 2101.

Saturated hydrocarbon gases at any desired pressure may be subjected to several arcs, the lengths of which are varied according to the changing composition of the gas.[38] As an illustration, the gases obtained during the hydrogenation of coal are passed through successive arcs 200, 280, and 350 mm. in length, the acetylene formed being removed after each arc. In other processes for the production of acetylene and hydrogen it has been suggested that the hydrocarbon gas be passed over the arc under reduced pressure,[38a] or conducted over it at such a rate that the ratio of the amount of gas in cubic meters per hour to the kilowatt power of the arc is between 0.6 and 1.6.[38b]

Several procedures described by Hull [39] involve the rapid passage of the hydrocarbon gases through the reaction zone in such a manner as to impart whirling motion or turbulence to the gases. One way in which this is obtained is by feeding a number of streams of gas to the arc, one of which distends the arc while the others impinge on one another. Another method is the creation of an electric discharge between a hollow conducting tube, having its mouth shaped convergently in the direction of gas flow, and an opposing rod electrode. The gas traveling along the hollow tube at a high velocity distends the electric discharge into the tube. When using high tension arcs the electrodes are made of, or tipped with, carbon. With low tension arcs Hull suggested electrodes consisting of tungsten, molybdenum, osmium, tantalum, or the carbides of these metals.[40]

Mercier [41] has proposed the following manner of operation, particularly for the conversion of liquid hydrocarbons into gases. An arc is struck while the two electrodes are in contact, and these are then separated from one another to the maximum extent consistent with the stability of the arc; or the oil is led through the center of hollow stationary electrodes, which have conical ends, thus allowing the spreading of the arc which jumps between them and the opposite insulated movable electrodes. The gases formed are simultaneously cooled by the oil pumped through the electrodes (a condition favoring the production of acetylene) and removed from the system by a vacuum pump. Yields of acetylene as high as 16 per cent are said to be obtained when the hydrocarbon oil, in a fine state of division, is conducted through a furnace so arranged that an electric arc formed therein has an energy consumption of 2 kilowatts per second per cubic centimeter of space.[42] Other methods for the conversion of liquid petroleum hydrocarbons to acetylene consist in spraying a stream of the oil alone[43] or mixed with hydrogen[44] into an electric arc.

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[38] Eisenhut, U. S. Patent 1,794,004, Feb. 24, 1931; *Chem. Abs.*, 1931, **25**, 2060; German Patent 540,897, 1926; *Chem. Abs.*, 1932, **26**, 2127; French Patent 674,459, 1929; *Chem. Abs.*, 1930, **24**, 2385; British Patent 337,088, 1929; *Chem. Abs.*, 1931, **25**, 1744; all patents assigned to I. G. Farbenindustrie A.-G. *Cf.* Eisenhut, U. S. Patent 1,904,426, April 18, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3409.

[38a] I. G. Farbenindustrie A.-G., British Patent 332,057, 1929; *Chem. Abs.*, 1931, **25**, 39.

[38b] I. G. Farbenindustrie A.-G., British Patent 332,917, 1929; *Chem. Abs.*, 1931, **25**, 462; French Patent 687,973, 1930; *Chem. Abs.*, 1931, **25**, 648; British Patent 336,261, 1929; *Chem. Abs.*, 1931, **25**, 1745.

[39] British Patent 311,352, 1928; *Brit. Chem. Abs.* **B**, 1929, 606. British Patent 317,538, 1928; *Brit. Chem. Abs.* **B**, 1929, 880. British Patent 317,558, 1928; *Chem. Abs.*, 1930, **24**, 2067. British Patent 317,920, 1928; *Brit. Chem. Abs.* **B**, 1929, 880. All patents assigned to Imperial Chemical Industries, Ltd. See also I. G. Farbenindustrie A.-G., British Patent 371,916, 1931; *Brit. Chem. Abs.* **B**, 1932, 633; French Patent 739,952, 1932; *Chem. Abs.*, 1933, **27**, 2101; British Patent 389,165, 1931; *Brit. Chem. Abs.* **B**. 1933, 377.

[40] British Patent 304,914, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.*, 1929, 274. See also Maillard, *Compt. rend. congr. graissage* 1931, 308.

[41] British Patents 316,336 and 316,352, 1928; *Brit. Chem. Abs.* **B**, 1929, 804. U. S. Patent 1,830,615, Nov. 3, 1931; assigned to Société l'air liquide; *Chem. Abs.*, 1932, **26**, 659.

[42] I. G. Farbenindustrie A.-G., British Patent 370,414, 1930; *Brit. Chem. Abs.* **B**, 1932, 586.

Coals, tars, resinous or asphaltic materials yield acetylene on treatment in an electric discharge according to a process which provides that the decrease from no-load to working tension is not more than 30 per cent.[45] If nitrogen is present, hydrogen cyanide is formed.

A number of procedures have been developed for the separation of acetylene from gaseous mixtures of hydrocarbons. These are discussed in Chapter 4. Two methods, however, may be mentioned. One of these, the mechanical separation of ethylene, is described by Eisenhut.[46] The gas mixture around the arc is composed of a zone rich in and a zone poor in acetylene. The former is withdrawn separately from the apparatus.

Another method of separation involves the use of selective organic solvents, particularly ketones.[47] The reaction gases are washed, best under pressure, and acetylene and other unsaturated hydrocarbons subsequently recovered by distillation of the solvent. In the aliphatic series, methyl ethyl ketone, methyl propyl ketone, diethyl ketone and diacetone can be employed and of the cyclic ketones, acetophenone, cyclohexanone, and methylcyclohexanones are recommended.

When hydrocarbon gases are exposed to the electric arc for a shorter period of time (i.e., at a higher rate of flow) than that required for acetylene formation the result is the production of higher olefins and diolefins.[48] For example, when ethylene (97 per cent purity) was passed at the rate of 40 liters per hour through an electric arc between carbon electrodes having a consumption of about 200 watts, the resulting gas mixture had the following composition: unsaturated hydrocarbons, 64.2 per cent; hydrogen, 29.9 per cent; methane, 3.6 per cent; and nitrogen, 2.3 per cent. Analysis indicated the unsaturated hydrocarbons to consist of the following:

	Per Cent by Weight
Unaltered ethylene	69.5
Propylene	15.0
Butylene	1.8
Butadiene	5.7
Acetylene	8.0

If the above operation be carried out continuously at a higher rate of flow and with continuous removal of the butadiene after formation, then higher yields of this diolefin are obtainable, accompanied by a reduction in the output of acetylene. Greater conversion of the olefin into butadiene may also be effected by prolonging the circulation of the gases, or by applying more electric energy.

Butadiene, together with other olefins and diolefins, is obtained when petroleum or mineral oils in the vaporized or finely divided state are conducted through electrical discharges at 700° to 800° C. Electrodes of copper or its alloys, chromium-nickel alloys, iron, or carbon seem to be particularly applicable for this type of conversion.[49] Olefins and diolefins may be produced also by leading the vapors of mineral oils through a bed of bituminous fuel heated electrically.[50] In this instance the fuel is placed in a fire-brick shaft having electrodes in the walls.

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[43] Nutting and Rowley, U. S. Patent 1,887,658, Nov. 15, 1932; assigned to Dow Chemical Co.

[44] Kipper, U. S. Patent 1,883,799, Oct. 18, 1932; assigned to R. B. Knox.

[45] I. G. Farbenindustrie A.-G., British Patent 365,045, 1930; *Chem. Abs.*, 1933, **27**, 1832.

[46] U. S. Patent 1,726,547, Sept. 3, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1929, **23**, 5121. Also British Patents 263,859 and 288;056, 1926; *Brit. Chem. Abs.* **B**, 1928, 415. *Cf.* Eisenhut, Schilling and Baumann, U. S. Patent 1,923,140, Aug. 22, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 5085.

[47] I. G. Farbenindustrie A.-G., 325,817, 1928; *Brit. Chem, Abs.* **B**, 1930, 449.

[48] I. G. Farbenindustrie A.-G., British Patent 315,249, 1928; *Brit. Chem. Abs.* **B**, 1929, 804.

[49] I. G. Farbenindustrie A.-G., British Patent 318,270, 1928; *Brit. Chem. Abs.* **B**, 1929, 882.

It has been pointed out that the efficiency of utilization of electrical energy in the manufacture of acetylene from hydrocarbons in the electric arc is increased by raising the current density of at least one of the electrodes to the point at which loss of material can be detected.[51] It has also been suggested that the electrical energy fed to the arc be such that the Balmer series of H lines be distinctly visible, at least to the Hδ line. It is recommended that the consumption of electrical energy be 2 kilowatts per cc. of space filled by the arc.[52]

As previously mentioned, acetylene is formed when a gaseous mixture of methane and hydrogen is subjected to the action of the electric arc. By adding nitrogen to the mixture both acetylene and hydrogen cyanide are produced simultaneously.[53] The mixture of hydrogen, nitrogen and methane is circulated through the arc until the concentration of the hydrogen cyanide is about 1 per cent and that of the acetylene about 2 to 3 per cent by volume. The reaction gases are then scrubbed with caustic soda solution and passed through active charcoal to remove the hydrogen cyanide and acetylene, respectively. The residual gases are returned to the system for recirculation.

Other methods for obtaining hydrogen cyanide by the reaction of hydrocarbons with nitrogen are discussed in Chapter 10.

Hydrogen, derived from the reaction between carbon monoxide and steam, is mixed with hydrocarbon gases and the mixture is washed with alkali carbonate solutions both before and after being subjected to the arc. The first alkali wash removes any carbon dioxide, and the second alkali wash absorbs hydrogen cyanide and any hydrogen sulphide formed in the arc. The bicarbonate solution resulting from the first wash may be decomposed by heating, and the carbon dioxide used to liberate hydrogen cyanide and sulphide from the second solution.[54]

Replacing the hydrogen in gaseous mixtures by steam or carbon dioxide results in the formation of acetylene, hydrogen, and carbon monoxide from these oxygen-containing gases and the hydrocarbons.[55] By mixing the initial gases in the correct proportions and then removing the acetylene after the reaction, a residual gas mixture of hydrogen and carbon monoxide applicable for the synthesis of methanol is made.

The action of electric arcs, sparks, or silent discharge on hydrocarbons, particularly olefins, in the presence of hydrogen and carbon monoxide has been suggested as a method for the synthesis of higher molecular compounds.[56] For example, butylene may be obtained from propylene in this manner, the reaction being represented by

$$C_3H_6 + 2H_2 + CO \longrightarrow C_4H_8 + H_2O$$

Similarly benzene is converted to its homologues. It is recommended that the electrodes be made of or tipped with iron, aluminum, copper, nickel, ferro-nickel, sodium or potassium or alloys of these metals and that the reaction be carried out at temperatures up to 500° C. and pressures as high as 30 atmospheres. Another procedure for the synthesis of higher hydrocarbons consists in subjecting gaseous mixtures of hydrogen, carbon monoxide, and saturated or unsaturated hydrocarbons to high frequency electrical oscillations together with or followed by a heat treatment at temperatures above 900° C.[57]

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[50] Winkler and Feiler, German Patent 490,563, 1928; addition to German Patent 457,179; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 2275.

[51] Soc. Chim. Ind. in Basle, British Patent 368.164, 1931; *Brit. Chem. Abs.* **B**, 1932, 410. Also French Patent 718,088, 1931; *Chem. Abs.*, 1932, **26**, 2662.

[52] I. G. Farbenindustrie A.-G., French Patent 717,608, 1931; *Chem. Abs.*, 1932, **26**, 2930.

[53] Andriessens, British Patent 296,355, 1928; assigned to Soc. Chem. Ind. in Basle; *Brit. Chem. Abs.* **B**, 1929, 507.

[54] Bückert and Baumann, German Patent 543,111, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2383.

[55] Soc. l'Air Liquide, French Patent 712,092, 1931; *Chem. Abs.*, 1932, **26**, 1866. British Patent 377,658, 1930; *Chem. Abs.*, 1933, **27**, 2389.

[56] Soc. anon. le pétrole synthétique, British Patent 223,543, 1924; *Chem. Abs.*, 1925, **19**, 1101; *J.S.C.I.*, 1925, 534B.

THE SILENT DISCHARGE

Although in certain severe cases the silent electric discharge has been found to split the C—C linkage in the molecule, the usual observed effect is dehydrogenation followed by polymerization through the nascent unsaturated valences. In this respect the effect of the silent discharge is similar to that obtained at high temperatures, as has been shown by Davis[58] to occur with acetone and benzol. The difference between the two cases, however, is that most of the material treated at high temperature is converted to lower molecular weight products, whereas in the silent electric discharge high yields of condensation and polymerization products are obtained.

Berthelot[59] reported that methane, ethane and ethylene when subjected to the silent discharge yielded a little acetylene, free hydrogen, and resinous condensation products. Ethane produced some free ethylene and a polymerized liquid of the approximate formula, $(C_{10}H_{16})_6$. Benzene was found to unite with two atoms of hydrogen and then form a polymer of dihydrobenzene, (C_6H_8), and oil of turpentine after absorbing 2.5 atoms of hydrogen also polymerized.

Later Berthelot[60] observed that methane, under the influence of the silent discharge, lost one-half of its hydrogen and yielded a solid hydrocarbon of the composition $C_{10}H_{18}$. In the presence of nitrogen, methane yielded a solid basic substance, C_2H_3N. This, Berthelot considered, as possibly a polymerized acetylenylamine. Similar results were obtained with ethane, a solid compound, $C_{10}H_{18}$, again being formed, though it was not identical with the substance derived from methane. Ethane in the presence of nitrogen was transformed into a solid basic material, $C_{16}H_{32}N_4$. Olefins, such as ethylene and propylene, gave solid hydrocarbons, and in the presence of nitrogen were changed to basic nitrogenous compounds. In each instance the products were of much higher molecular weight than the initial hydrocarbon, indicating that after first losing hydrogen the molecule must have undergone considerable polymerization and condensation. Acetylene, under similar conditions, produced no hydrogen, but was changed first to a liquid and then to a solid. The latter was rapidly oxidized on exposure to air, and decomposed violently when heated. In the presence of nitrogen, the solid compound, $C_{18}H_{16}N_2$, was formed.

Losanitsch and Jovitschitsch[61] noted that ethylene was polymerized by the silent discharge (3.5 amperes at 70 volts) to a thick yellow liquid boiling above 200° C. This substance absorbed oxygen readily, forming a viscous oil[62] having a composition corresponding to $(C_{12}H_{22}O)_2$. Similarly equal volumes of ethylene and methane condensed to a clear, yellow, viscous liquid. The latter also absorbed oxygen, yielding the compound $C_{22}H_{42}O_4$. Under the same conditions ethylene and hydrogen sulphide quickly condensed to form the compound $(C_2H_4S)_6$, a yellowish-red liquid with a mercaptan-like odor. The reactions yielding the latter are probably

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[57] Ruhrchemie A.-G., British Patent 355,210, 1929; *Chem. Abs.*, 1932, 26, 4065; French Patent 690,028, 1930; *Chem. Abs.*, 1931, 25, 962.

[58] *J. Phys. Chem.*, 1931, 35, 3330. *Cf.* Harkins and Gans, *J.A.C.S.*, 1930, 52, 5165.

[59] *Bull. soc. chim.*, 1876, (2) 26, 101; *J.C.S.*, 1876, 30, 596. *Bull. soc. chim.*, 1876, (2) 26, 98; *J.C.S.*, 1876, 30, 617.

[60] *Compt. rend.*, 1898, 126, 561, 567, 609, 616; *Chem. Soc. Abs.*, 1898, 74 (1), 393. This investigation included not only the effect of the silent discharge on hydrocarbons, but also on many organic compounds such as carbon dioxide, alcohols, phenols and others.

[61] *Ber.*, 1897, 30, 135.

[62] Losanitsch, *Ber.*, 1907, 40, 4656. *Monatsh.*, 1908, 29, 753.

$$C_2H_4 + H_2S \longrightarrow CH_3CH_2SH$$
$$6CH_3CH_2SH \longrightarrow (C_2H_4S)_6 + 6H_2$$

Some evidence for such reactions was that ethyl mercaptan when subjected to the silent discharge also gave the compound $(C_2H_4S)_6$.

When using slightly more energy (3 amperes and 100 volts) Jovitschitsch[63] obtained from ethylene the substance, $C_{30}H_{54}$, which he considered to be a cyclic compound. When treated with nitric acid at 50° to 60° C., two nitro compounds were obtained. The first, having the formula $C_7H_{11}NO_2$, was soluble in hot alcohol, and the second, $C_6H_9NO_2$, was insoluble. Thénard[64] observed that ethylene was similarly condensed to a liquid possessing a strong odor and soluble in ether but insoluble in water. Methyl ether decomposed yielding 1 volume of methane and 2 volumes of hydrogen, a strong acid. and a resinous substance. The latter was soluble in alcohol but insoluble in ether.

Somewhat more information concerning the polymerization products from ethylene has been furnished by Collie.[65] The liquid obtained after this olefin was treated for a considerable length of time with the silent discharge was fractionated. A small amount distilled below 100° C., and the greater part came over between 100° C. and 250° C. (more than half below 175° C.). A large proportion (about 40 per cent) of resinous material was left as a residue. Analysis of the fractions indicated they were mixtures of C_nH_{2n} hydrocarbons containing from 6 to 15 carbon atoms. From the lowest boiling fraction there was also isolated a substance which, from its chemical reactions, appeared to be a polymerized compound. Collie suggested that under the influence of the silent discharge ethylene yields hydrocarbons having the approximate formula, $C_{10}H_{20}$. These lose hydrogen and polymerize to substances having properties somewhat like india-rubber and compositions very close to $(C_5H_8)_n$.

Stratta and Vernazza[66] also noted that a variety of products were obtained from ethylene. They believed these to be the result of (a) direct condensation of two or more molecules of ethylene, (b) transformation to double and triple bonded condensation products, or (c) the formation of ethane or methane and its homologues from interaction of liberated hydrogen and unsaturated hydrocarbons. These investigators also found that the condensation of ethylene is proportional to the concentration of ethylene and the net rate of acetylene formation from ethylene decreases rapidly with the time as a result both of diminution in concentration of ethylene and secondary condensation of acetylene. According to Szukiewicz,[67] acetylene is converted by the action of the silent discharge into ethylene, erythrene, diacetylene, butane, hexane and other hydrocarbons.

Volmar and Hirtz[68] studied the hydrogenation of ethylene in an electric discharge. A slow stream of ethylene and hydrogen (at 20 mm.) was submitted to the silent discharge. The reaction velocity and yield of saturated hydrocarbons increased proportionately to the concentration of hydrogen. Methane was the chief product, but some ethane and propane were also obtained. It was suggested that the primary reaction is the breaking up of ethylene into CH_2 radicals which then react with hydrogen to give methane, or with a second molecule of ethylene to yield (after hydrogenation) propane, or decompose to carbon and hydrogen. Acetylene under similar conditions gave acetylene hydrocarbons containing as high as 10 carbon atoms and saturated hydrocarbons up to 8 carbon atoms. Volmar and Hirtz concluded that activated hydrogen was probably the hydrogenating agent.

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[63] *Monatsh.*, 1908, **29**, 5.

[64] *Compt. rend.*, 1873, **76**, 1508; *Chem. Soc. Abs.*, 1873, **26**, 1093.

[65] *J.C.S.*, 1905, **87**, 1540. For the use of the silent discharge to polymerize ethylene to oily products, see I. G. Farbenindustrie A.-G., British Patent 353,404, 1929; *Chem. Abs.*, 1932, **26**, 3446.

[66] *Industria chimica*, 1931, **6**, 133; *Chem. Abs.*, 1931, **25**, 4186; *Industria chimica*, 1933, **8**, 698; *Brit. Chem. Abs.* **A**, 1933, 804.

[67] *Rocz. Chem.*, 1933, **13**, 245; *Chem. Abs.*, 1933, **27**, 4487.

[68] *Bull. soc. chim.*, 1931, **49** (4), 684; *Brit. Chem. Abs.* **A**, 1931, 932.

When working under conditions which allowed the products of the reaction to be withdrawn rapidly, Mignonac and Vanier de Saint-Aunay[69] observed that the primary product was 1-butene and from this 1-hexene was formed. They represented the reactions by:

$$(1)\quad CH_2{=}CH_2 + H\cdot CH{=}CH_2 \longrightarrow CH_3CH_2CH{=}CH_2$$

$$(2)\quad CH_3CH_2CH{=}CH_2 + H\cdot CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CH_2CH{=}CH_2$$

Low temperatures (—80° C.) favored the yield of 1-butene and raising the temperature increased the yield of 1-hexene. This formation of higher molecular weight hydrocarbons from ethylene had been observed also by Demjanov and Prianischnikov,[70] who obtained a yellow mobile oil (d^{20}_{4} 0.8360 and average molecular weight of 215) when using a silent discharge of 12,000 to 13,000 volts. The oil was thought to contain unsaturated hydrocarbons consisting of hexene (C_6H_{12}) and higher.

The latter investigators also reported that isobutylene gave a product having an average molecular weight of 140 and d^{20}_{4} 0.822, which was composed of principally C_8H_{16} and $C_{12}H_{24}$ hydrocarbons. Later Prianischnikov[71] investigated some of the fractions from distillation of the product. Two fractions in particular, one boiling between 32° and 52° C. and the other between 75° and 85° C., were mixtures containing about 20 to 30 per cent of unsaturated hydrocarbons (C_nH_{2n}) and 70 to 80 per cent of saturated hydrocarbons (C_nH_{2n+2}). 2,2-Dimethylbutane and 2,3-dimethyl-2-butene were probably present in the first fraction, and 2,2- and 2,4-dimethylpentanes and 2,2,3-trimethylbutane, in the second. Fractions of higher boiling points were richer in unsaturated hydrocarbons and also contained some naphthenes. The reactions produced by the silent electric discharge are apparently not only simple polymerization, but are also accompanied by a redistribution of the hydrogen atoms. These effects are somewhat similar to those observed by Ipatiev when ethylene was subjected to high temperatures and pressures (see Chapter 2). Prianischnikov also noted that the properties of the products were influenced by the duration of the discharge (time factor).

Amylene vapor, when mixed with hydrogen, and treated with an electrical discharge in an ozonizer, was converted (about 85 per cent) into liquid products in which saturated hydrocarbons of the C_5H_{12} type (or isomers) predominated.[72] Some unsaturated hydrocarbons, such as isopropylacetylene, were also found. The gaseous products were acetylene, allylene, vinylacetylene and diacetylene. Alone or mixed with nitrogen, no saturated hydrocarbons were produced from amylene. The hydrogen appeared to act not only as a hydrogenating but also as a dehydrogenating agent, uniting with a hydrogen atom of the unsaturated hydrocarbon and bringing about unions of the resulting hydrocarbon residues. This would explain the formation of compounds with double the number of carbon atoms. Amylene also appears to undergo a number of other transformations, including bond transpositions, rearrangements, cyclicization, molecular cleavage, formation of simple and multiple bonds, and polymerization. From their data Meneghini and Sorgato were unable to differentiate between these various transformations. In addition, under the experimental conditions, reactions take place which lead to an increase in internal energy, and therefore the endothermic character of the triple bond brings about the formation of large quantities of acetylenic hydrocarbons. When a discharge tube producing a corona effect was employed the proportion of amylene transformed was much less, though the changes were more deep-seated and separation of free carbon occurred.

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[69] *Compt. rend.*, 1929, **189**, 106.

[70] *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 462; *Brit. Chem. Abs.* **A**, 1927, 336.

[71] *Ber.*, 1928, **61**, 1358.

[72] Meneghini and Sorgato, *Gazz. chim. ital.*, 1932, **62**, 621; *Chem. Abs.*, 1933, **27**, 58.

According to Koenig,[73] the action of the silent electric discharge on gases is a very complicated process in which primary and secondary reactions take place almost simultaneously. The layer of gas close to the wall of the reaction tube remains practically undisturbed, even with rapid flow, and is not carried away, thus remaining exposed to the further action of the discharge. This difficulty can be overcome, at least in part, by washing the wall of the reaction tube with a liquid. In this way, for example, much better yields of formaldehyde[74] may be obtained in the electrical treatment of water gas, if the reaction chamber is flushed every few minutes with water which washes the formaldehyde from the walls, thus avoiding its destruction by the electric discharge. Similarly with the aid of a reflux condenser attached to the discharge tube, it is possible to obtain the primary products of the electrical decomposition of hydrocarbons (e.g., diphenyl from benzene and diphenylmethane from toluene) without subjecting these materials to further change. Koenig also pointed out that the primary effect of the electron bombardment of the gas molecules consists (1) in loosening, or in tearing off, electrons (ionization), (2) in disintegrating the disrupted molecules provided they do not emit their surplus energy as light waves, and (3) in condensing the unsaturated residues, which are the result of this disturbance, to yield new substances.

Acetylene is readily polymerized when subjected to the silent discharge. Thus Losanitsch[75] converted acetylene into a viscous or solid mass which could be separated with alcohol or ether into soluble and insoluble portions. The soluble portion was a viscous, fragrant oil, which rapidly absorbed oxygen, yielding the substance $(3C_2H_2.C_2H_4.O)_5$. The insoluble solid portion, of the formula $C_{48}H_{46}$, had a very disagreeable odor and absorbed oxygen to give the compound $C_{48}H_{40}O_8$. Both of these oxygen derivatives yielded an emanation which liberated iodine from a potassium iodide solution and through aluminum or gold leaf affected a photographic plate. Losanitsch did not consider this emanation to be radioactive in character, but rather to result from the absorbed oxygen present in a labile state. He also noted that acetylene, in the presence of the silent discharge, could be condensed with other substances such as hydrogen, methane, ethylene, hydrogen sulphide, carbon monoxide, and sulphur dioxide.

Jovitschitsch[76] considered the product obtained from acetylene to have the formula $C_{30}H_{26}$. From this he was able to prepare di-, tri-, and tetrabromides ($C_{30}H_{26}Br_2$, $C_{30}H_{25}Br_3$, and $C_{30}H_{24}Br_4$, respectively) and with fuming nitric acid apparently a trinitro compound, $C_{30}H_{25}O_{30}N_3$.

Later, Kaufmann[77] pointed out that the reaction product is a liquid when the apparatus is kept cold, but a mixture of a solid and a liquid when warm. On dissolving the liquid product in ethyl ether and warming (to about 60° C.) the same solid can be obtained. The liquid is a brown viscous oil of unpleasant odor, having the composition $(C_2H_2)_n$. On distilling, a small portion comes over at 70° C. (10 mm. pressure), the remainder carbonizing or changing to a plastic mass which ultimately becomes solid. The solid is a pale yellow, odorless powder, insoluble in all solvents. Both the liquid and solid compounds can be oxidized, the former much more readily than the latter. On oxidation they both yield benzoic, isophthalic, and terephthalic acids. The liquid product forms a pale yellow precipitate with alcoholic silver nitrate, indicating the presence of the $—C{\equiv}CH$ grouping. The action of the oxygen derivatives of both the solid and liquid substances on a photographic plate was observed, but it was further noted that this action occurred only while the absorption of oxygen was actually taking place.

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[73] *Chem. Ztg.*, 1928, 787.

[74] I. G. Farbenindustrie A.-G., British Patent 304,623, 1927; *Chem. Abs.*, 1929, 23, 4628.

[75] *Ber.*, 1907, 40, 4656.

[76] *Monatsh.*, 1908, 29, 5.

[77] *Ann.*, 1918, 417, 34; *Chem. Abs.*, 1919, 13, 1825.

Mignonac and Vanier de Saint-Aunay,[78] in experiments at low temperatures (—60° C.), observed that acetylene was polymerized mainly to a trimer, boiling at —10° C. and having a $d^{19.5}_{4}$ 0.752. This trimer slowly underwent further polymerization. When oxidized with permanganate it yielded formic, oxalic, propionic, and succinic acids. It also formed an ozonide which on hydrolysis gave formaldehyde. Reactions of the trimer with alcoholic silver nitrate or cuprous chloride indicated that it might be a mixture of (1) dipropargyl, (2) 3-methyl-1,4-pentadiine $(CH{\equiv}CCH(CH_3)C{\equiv}CH)$ and (3) divinylacetylene $(CH_2{=}CHC{\equiv}CCH{=}CH_2)$.

The paraffin hydrocarbons also disintegrate under the action of the silent discharge. Thus, Lind and Glockler[79] found that when ethane was submitted to a silent discharge of 12,000 volts in a Siemens ozonizer tube, through which the gas was continuously circulated by means of an all-glass magnetic pump, most of the ethane was decomposed in 3 hours, yielding a gas consisting mainly of hydrogen, methane, and propane with smaller amounts of higher homologues. At the same time as much as 45 to 55 per cent of the ethane was converted into a viscous, reddish-yellow oil of density 0.862 and n^{20} 1.490. This oil had the composition: carbon 85.48 per cent and hydrogen 13.09 per cent. Its apparent molecular weight in benzene was 467, and it readily formed substitution products with bromine. The action of the silent discharge was very similar to that produced by α-particles from radon. Later, Lind and Glockler[80] showed that it was possible to regulate the molecular weight of the liquid product obtained by the action of the silent discharge, corona, and high-frequency discharge on ethane by removing the liquid reaction products from the walls of the reactor. By thus controlling the time that the initial products, either gaseous or liquid, were allowed to remain under the influence of the discharge, the average molecular weights of the liquids formed could be regulated between 105 and 467. The secondary action took place the more the higher the molecular weight of the substances produced by further condensation.

These same investigators[81] extended their work to include methane, propane, butane and ethylene. The results with these hydrocarbons were analogous to those obtained with ethane; that is, the action of the silent discharge resulted in the formation of hydrogen, higher homologues of the paraffin series, and a liquid condensate corresponding in formula to C_nH_{2n}. Comparing these data with those obtained with α-rays led to the conclusion that "for all of the hydrocarbons studied the condensations by alpha rays and in electrical discharge have many points in common, which lead to the belief that they both are brought about by the same agency." Comparison of the product of the M/N values (ratio of the number of reacting molecules to the number of ion pairs) and the molar ionization also indicates a similarity between the α-ray and electrical condensations.[82]

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[78] *Compt. rend.*, 1929, **188**, 959; *Chem. Abs.*, 1929, **23**, 3437.

[79] *Trans. Amer. Electrochem. Soc.*, 1927, **52**, 37.

[80] *J.A.C.S.*, 1928, **50**, 1767.

[81] Lind and Glockler, *J.A.C.S.*, 1930, **52**, 4450. For the production of acetylene from methane by silent discharges, see Institut für physikalische Grundlagen der Medizin, British Patent 362,869, 1930, addition to British Patent 340,862; *Chem. Abs.*, 1933, **27**, 1421.

Vanier de Saint-Aunay[83] found that by rapid circulation and intense cooling of the gases, the action of high-frequency and low-frequency discharges can be made to yield definite compounds. Methane may be dehydrogenated to give hydrogen and free radicals, the latter condensing for the most part to ethane. Ethane, by dehydrogenation, yields ethylene and acetylene or it may undergo scission of its carbon atoms and the products formed then react further with hydrogen to form methane. Ethylene polymerizes to 1-butene and 1-hexene or is dehydrogenated to acetylene. By reaction with liberated hydrogen ethylene is also converted into ethane, butane and hexane. Benzene through polymerization gives dihydrobiphenyls, and by dehydrogenation, diphenyl, or by depolymerization it may yield acetylene, which on reacting with liberated hydrogen produces ethylene and ethane.

Investigation of the effect of pressure[84] on the reaction brought out the following facts: With constant duration of discharge (1 hour) the percentage of methane reacting and of free hydrogen produced increased rapidly with decrease in pressure; (2) the proportion of liquid products formed also increased with decreasing pressures; and (3) appreciable quantities of unsaturated hydrocarbons were obtained only at pressures greater than 200 mm. When the pressure was kept constant and the duration of the discharge varied, it was observed that with methane a steady state of synthesis and decomposition of the hydrocarbon was attained after 20 minutes and that further action of the discharge resulted in an increased yield of liquid products and of hydrogen. This induction period of 20 minutes was not noted with ethylene, but if such a period did exist it must have been much shorter. In comparing the percentages of hydrocarbons which had reacted when subjected to the discharge for 1 hour, it was found that for methane this corresponded to about 23 per cent, for ethylene about 85 per cent, and for acetylene 100 per cent. In addition, during the condensation of acetylene it was noted that some of the hydrocarbon was hydrogenated, probably to ethane or ethylene.

Lind and Glockler[85] studied the action of a semi-corona discharge (using a central aluminum rod in a pyrex glass cylinder) on methane, ethane, propane, butane, and ethylene. They found that condensation to liquid and solid hydrocarbons occurred in every case. With saturated hydrocarbons, condensation is brought about by elimination of hydrogen and some methane. These reactions are of the general character of those produced in the same gases by α-radiation. The liquids obtained at the same temperatures from different hydrocarbons exhibited similar physical properties, but these properties could be varied by changing the temperature of the discharge regions and the traps in which the liquids were collected.

The liquids from the action of the silent discharge on butane were examined in some detail.[86] The apparatus consisted of twelve glass ozonizers connected in parallel, the voltage employed being 20,000 volts. Butane (5420 grams) was passed continuously through the apparatus for a period of 660 hours and 1041 cc. of a liquid condensate (density 0.804) were secured. This was equivalent to a 15.37 per cent conversion of the butane. The liquid was separated into 40 fractions by distillation (at various pressures), and these were light, medium, and very viscous oils. One of the light fractions (the larger portion of the light oils) possessed the following properties:

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[82] Lind and Schultze, *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 141.

[83] *Chimie et industrie*, 1933, **29**, 1011; *Chem. Abs.*, 1933, **27**, 3911.

[84] Lind and Schultze, *J.A.C.S.*, 1931, **53**, 3355.

[85] *J.A.C.S.*, 1929, **51**, 2811. The description of an apparatus for the electrical treatment of hydrocarbon gases and vapors is given by Rowland, U. S. Patent 1,837,489, Dec. 22, 1931; assigned to Corona Conversion Corp.; *Chem. Abs.*, 1932, **26**, 1202.

B.P.	110° to 114° C.
N^{20}	1.4021
D^{20}_{4}	0.708
Molecular weight	114.7
Carbon	84.55%
Hydrogen	15.45%
Empirical formula	$C_8H_{17.4}$
Unsaturation (by halogenation)	22.5 mole per cent

This fraction was recognized as a mixture of octane and octylenes.

It is of interest to note that this largest fraction of light oils consisted of 8-carbon-atom molecules which can be produced from butane by simple doubling according to the Lind[87] theory of ionic reactions. The reactions can be formulated as follows:

$$C_4H_{10} \longrightarrow C_4H_{10}^{+} + E \text{ (ionization)}$$
$$C_4H_{10} + C_4H_{10}^{+} \longrightarrow (C_4H_{10}.C_4H_{10}) + \text{ (clustering)}$$
$$(C_4H_{10}.C_4H_{10})^{+} + E \longrightarrow C_8H_{18} + H_2 \text{ (neutralization of the cluster and rearrangement of bonds)}$$

Becker[88] reported that paraffin hydrocarbons when subjected to a high-tension discharge in a Siemens ozonizing tube yielded hydrogen and higher paraffins. This general reaction may be represented by

$$C_nH_{2n+2} + C_mH_{2m+2} \longrightarrow C_{n+m}H_{2(n+m)} + H_2$$

Methane gave only a small proportion of liquid hydrocarbons. Under the same conditions unsaturated hydrocarbons were converted to mixtures of saturated hydrocarbons of high molecular weights. Cyclic compounds behaved in a complex manner, since mixtures of saturated and unsaturated hydrocarbons were formed from the degradation products of the original substances. For example, decahydronaphthalene yielded butane, small quantities of unsaturated hydrocarbons, and about 25 per cent of resinous products of high molecular weight.[89]

The production of lubricating oils with improved properties by subjecting mineral oils or mixtures of fatty and mineral oils to the action of silent electric discharges has been brought to commercial success at several places in Europe.[90] About 1906, de Hemptinne[90a] showed that viscous oils result from the treatment of fatty oils with such discharges. Researches were extended to the action of these discharges on mineral oils, similar changes being observed.[90b] The process was called voltolization and the various viscous products thus formed were called voltols, voltolized oils, or "Elektrion" oils. It is stated that voltolized oils show less change in viscosity with temperature (i.e., give flatter viscosity curves) than ordinary lubricating oils and do not differ appreciably in acid number, asphalt content or cold test; hence they have been employed (usually in admixture with ordinary lubricating oil) as substitutes for castor oil in airplane lubrication.[90c] According to Wolf,[90d] in the production the mineral oil is allowed to flow over aluminum electrodes where it is exposed to a high-frequency alternating current of 5000 volts, oxidation being prevented by an atmosphere of inert gas. Numerous modifications of this voltolization treatment have been suggested.[90e]

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[86] Lind and Glockler, *J.A.C.S.*, 1929, 51, 3655.

[87] S. C. Lind, "The Chemical Effect of α-Particles and Electrons" (2nd edition), Chemical Catalog Co., Inc., New York, 1928.

[88] *Wiss. Veröff. Siemens-Konz.*, 1929, 8, 199; *Chem. Abs.*, 1930, 24, 1803.

[89] For an explanation of this C+H "deficit" of the products of the action of the electric discharge on hydrocarbons, see Jovitschitsch, *Rad.*, 1929, 236, 233; *Brit. Chem. Abs.* A, 1931, 819.

[90] Otto, *Petroleum Eng.*, 1931, 2 (4), 112; *Chem. Abs.*, 1931, 25, 4392; Wolf, *Petroleum Z.*, 1929, 25, 95; *Chem. Abs.*, 1929, 23, 4563. See Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 1930, 616, *et seq.* *Cf.* Ellis and Wells, "The Chemical Action of Ultraviolet Rays," Chemical Catalog Co., Inc., New York, 1925, 332.

[90a] Various suggestions of de Hemptinne for treatment of oils with silent discharges are embraced in the following articles and patents: *Z. physik. Chem.*, 1897, 22, 360; *Chem. Soc. Abs.*, 1897,

Epner[91] suggested the manufacture of motor or power fuels by subjecting gaseous hydrocarbons to the prolonged action of an alternating current of high frequency and high tension. The liquids so made can then be rendered more stable chemically by hydrogenation.

Use of the corona discharge in vapor phase cracking is said to result in a greater yield of gasoline of higher antiknock value.[91a] The experimental plant in which this method was perfected had a small wire suspended in the reaction chamber as one electrode. The oil vapors were subjected to the action of a high tension alternating current discharge of frequency not exceeding 10,000 cycles per second.

The experiments of Jakowsky[92] indicated that the corona discharge (low frequency of 60 cycles) had no effect on vapor phase cracking below 600° C. Above this temperature, however, the use of a corona discharge gave a gasoline

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72, (2), 303; *Z. physik. Chem.*, 1898, **25**, 284; *Chem. Soc. Abs.*, 1898, **74** (2), 281; *Bull. acad. roy. Belg.*, 1911, **25**, 842; *ibid.*, 1912, **26**, 55; *Chem. Abs.*, 1912, **6**, 2857; *Bull. acad. roy. Belg.*, 1919, **5**, 161, 249, 521; *ibid.*, 1921, **7**, 146, 458, 590; *Chem. Abs.*, 1923, **17**, 2815. U. S. Patent 852,662, May 7, 1907; *Chem. Abs.*, 1907, **1**, 2188; U. S. Patent 970,473, Sept. 20, 1910; *Chem. Abs.*, 1910, **4**, 3168. British Patent 1,572, 1905; *J.S.C.I.*, 1905, **24**, 448; British Patent 7,101, 1905; *J.S.C.I.*, 1905, **24**, 663; British Patent 12,525, 1905; *J.S.C.I.*, 1906, **25**, 80; British Patent 13,023, 1906; *Chem. Abs.*, 1907, **1**, 2956; British Patent 15,748, 1909; *Chem. Abs.*, 1911, **5**, 33; British Patent 15,035, 1912; *Chem. Abs.*, 1914, **8**, 242; French Patent 376,111, 1907; *J.S.C.I.*, 1907, **26**, 971; French Patent 363,078, 1906; *Chem. Abs.*, 1906, **1**, 2956; French Patent 440,843, 1909; *J.S.C.I.*, 1910, **29**, 222; German Patent 185,931, 1904; *Chem. Abs.*, 1907, **1**, 3074; German Patent 234,543, 1909; *Chem. Abs.*, 1911, **5**, 2941; German Patent 236,294, 1909; *Chem. Abs.*, 1912, **6**, 1225; German Patent 251,591, 1911; *Chem. Abs.*, 1913, **7**, 698.

[90b] Hock, *Z. Elektrochem.*, 1923, **29**, 111; *J.S.C.I.*, 1923, **42**, 508A; *Kautschuk*, 1926, 65-7; *Chem. Abs.*, 1926, **20**, 2095; *Kautschuk*, 1930, **6**, 142; *Chem. Abs.*, 1930, **24**, 4661; Eichwald, *Z. angew. Chem.*, 1922, **35**, 505; *Chem. Abs.*, 1923, **17**, 60; *Vogel, Z. angew. Chem.*, 1922, **35**, 561; *Chem. Abs.*, 1923, **17**, 318; Zakharenko, *Neft. Khoz.*, 1929, **16**, 547; *Chem. Abs.*, 1929, **23**, 4809; Grossmann, *Allgem. österr. Chem. Tech. Ztg.*, 1927, **45**, 117; *Chem. Abs.*, 1928, **22**, 160; Fachini, *Atti II. congresso naz. chim. pura applicata*, 1926, 514; *Chem. Abs.*, 1928, **22**, 2264; Brückner, *Chem.-Ztg.*, 1928, **52**, 637; *Chem. Abs.*, 1928, **22**, 3981. Anon., *Petroleum Times*, 1922, **7**, 478; *Chem. Abs.*, 1922, **16**, 2219; Steinitz, *Chem. Ztg.*, 1930, **54**, 837; *Chem. Abs.*, 1931, **25**, 806; Vogel, *Autotech.*, 1932, **35**, 381; *Chem. Abs.*, 1932, **26**, 5746; *Erdöl u. Teer*, 1927, **3**, 534; *Chem. Abs.*, 1927, **21**, 4056; Eichwald, *Z. angew. Chem.*, 1923, **36**, 611; *Chem. Abs.*, 1924, **18**, 1049; *Z. deut. Oel-Fett-Ind.*, 1924, **44**, 241; *Chem. Abs.*, 1925, **19**, 1061.

[90c] Vogel, *Z. angew. Chem.*, 1922, **35**, 561; *Chem. Abs.*, 1923, **17**, 318; *Physik Z.*, 1921, **22**, 645; *Chem. Abs.*, 1923, **17**, 2661; Nash, *Proceedings Third International Conference on Bituminous Coal*, Nov. 16-21, 1931, 928.

[90d] *Petroleum Z.*, 1929, **25**, 95; *Chem. Abs.*, 1929, **23**, 4563. *Cf.* also Decavel and Roegiers, *Chimie et Industrie*, Special No., March 1931, 443; *Chem. Abs.*, 1931, **25**, 3575.

[90e] Rhenania-Ossag Mineralölwerke A.-G., German Patent 490,010, 1924; *Chem. Abs.*, 1930, **24**, 2013; German Patent 514,320, 1923; *Chem. Abs.*, 1931, **25**, 1167; German Patent 536,100, 1924; *Chem. Abs.*, 1932, **26**, 1114; Vogel, U. S. Patent 1,621,143, Mar. 15, 1927; *Chem. Abs.*, 1927, **21**, 1415; British Patent 254,375, 1925; assigned to Oelwerke Sternsonneborn A.-G.; *Chem. Abs.*, 1927, **21**, 2438; Siemens-Halske A.-G., German Patent 446,813, 1923; *Chem. Abs.*, 1929, **23**, 1577; I. G. Farbenindustrie A.-G., French Patent 654,650, 1928; *Chem. Abs.*, 1929, **23**, 3806; French Patent 702,198, 1930; *Chem. Abs.*, 1931, **25**, 4117.

[91] British Patent 294,100, 1927; *Chem. Abs.*, 1929, **23**, 2020; British Patent 294,099, 1927; *Chem. Abs.*, 1929, **23**, 2030; British Patent 296,019, 1927; *Chem. Abs.*, 1929, **23**, 2076; British Patent 295,705, 1927; *Chem. Abs.*, 1929, **23**, 2188; British Patent 317,344, 1928; *Chem. Abs.*, 1930, **24**, 2273.

[91a] Rowland, *Oil and Gas J.*, 1930, **29** (28), 38; *Chem. Abs.*, 1931, **25**, 805. U. S. Patent 1,779,402, Oct. 21, 1930; assigned to C. and C. Developing Co.; *Chem. Abs.*, 1931, **25**, 200.

[92] *U. S. Bur. Mines, Tech. Paper* **375**, 1926; *Brit. Chem. Abs.* **B**, 1927, 547.

with a higher percentage of unsaturated hydrocarbons. A larger proportion of fixed, or difficultly condensible, gases were obtained when a high-frequency discharge was employed. The discharge itself produced no cracking of the oil vapors. The increased cracking appeared due to precipitation of the hot oil vapors against the walls of the reaction chamber, and to the decrease in channelling of the vapors by the electric turbulence set up by the discharge.

THE DECOMPOSITION OF HYDROCARBONS BY OTHER FORMS OF ENERGY

Under this heading will be discussed briefly the decomposition of hydrocarbons by forms of energy other than those already mentioned. These include ultraviolet light, α-radiation, and excited mercury atoms.

Tolloczko[93] observed that methane was unaffected by light from a mercury vapor lamp. Ethane, however, yielded methane and hydrogen together with a small quantity of liquid condensate which analysis indicated to be a mixture of hydrocarbons, principally hexanes. Berthelot and Gaudechon[94] found that ethylene and acetylene were polymerized under these conditions. The former yielded a liquid, boiling below 100° C. and possessing a disagreeable odor. Acetylene gave a solid polymer, but no benzene or hydrogen. Allene, methylacetylene and isoprene are converted into white polymerides by radiation from the hot mercury arc.[95]

Kemula[96] reported that although no dissociation of methane takes place under radiation with a mercury-vapor lamp, under analogous conditions ethane yielded hydrogen, methane, butane, hexane and a small amount of unidentified saturated and unsaturated liquid hydrocarbons. The products of photolysis and their relative proportions varied with the duration of irradiation. The reaction was best represented by

$$\mathrm{nC_2H_6} \longrightarrow \mathrm{(n-1)H_2 + C_{2m}H_{4n+2}}\ \text{(liquid)}.$$

indicating that there is a volume contraction.

Experiments on the action of excited mercury atoms on pentane vapors were carried out by Frankenburger and Zell.[97] They found that the primary action consisted in a loosening of the C—H or C—C linkages. The liberated hydrogen atoms and free hydrocarbon radicals then underwent secondary reactions (1) with one another, in the presence of an inert (oxygen-free) atmosphere, to give hydrogen and higher and lower molecular weight hydrocarbons, and (2) in the presence of oxygen to form hydrogen peroxide and organic oxygenated compounds having $\mathrm{CH_3{\cdot}CO}$ and $\mathrm{CH_3{\cdot}C(OH)}$ groups.

This activation of the carbon-to-carbon or carbon-to-hydrogen linkages has also been observed with ethane.[98] This hydrocarbon, on irradiation with ultraviolet light in the presence of mercury vapors, gave butane, hexane and octane, together with some methane. The proportions of butane in the product varied directly with the rate of flow of gas and the pressure, and inversely as the temperature of the receiver. The rate of activation, however, was independent of the pressure or rate of flow, but depended exclusively on the intensity of radiation.

Attention has been directed toward the action of α-radiation on hydrocarbons, and it has been shown that even such stable hydrocarbons as methane can be

[93] *Przemysl Chem.*, 1927, 11, 245; *Chem. Abs.*, 1928, 22, 4380.

[94] *Compt. rend.*, 1910, 150, 1171. See also Landau, *Compt. rend.*, 1912, 155, 403.

[95] Lind and Livingston, *J.A.C.S.*, 1933, 55, 1036.

[96] *Rocz. Chem.*, 1930, 10, 273; *Brit. Chem. Abs.* A, 1930, 887.

[97] *Z. phys. Chem.*, 1929, 2, 395; *Chem. Abs.*, 1929, 23, 3206.

[98] Kemula, Mrazek and Tolloczko, *Chem. Listy*, 1932, 26, 466; *Brit. Chem. Abs.* A, 1932, 1215.

disrupted with the production of higher hydrocarbons. Mund and Koch[99] studied the action of radon on methane, ethane, ethylene and acetylene. They concluded that a reaction occurred with methane which resulted in diminishing the number of gaseous molecules. The substances formed were not identified. Ethane decomposed giving hydrogen and ethylene, the latter being converted to liquid or solid substances. Ethylene itself was slowly changed into liquid materials, and acetylene to a fine yellow-brown powder.

Lind and Bardwell,[100] in an extensive investigation of the action of α-radiation on saturated hydrocarbons, showed that ethane, propane and butane each condense to give higher hydrocarbons, which are gaseous, liquid or solid, and saturated or unsaturated. This condensation is preceded by the elimination of hydrogen and methane (in the approximate ratio of $5H_2:1CH_4$) from the hydrocarbon molecule. Analysis of the liquid products indicated the presence of a large proportion of unsaturated hydrocarbons, but no unsaturated hydrocarbons were found among the gaseous products. This was accounted for by the rapid polymerization (and therefore removal from the gas phase) of any unsaturated hydrocarbons formed. The higher the molecular weight of the paraffin the greater the yield of liquid materials, which were similar to those obtained by the action of the silent discharge. Methane also gave higher hydrocarbons, but the formation of these was accompanied by the elimination of hydrogen only.

The action of α-particles on acetylene was somewhat easier to determine and follow.[101] This hydrocarbon at ordinary temperatures and pressures polymerized to a light yellow powder, which in some respects resembled the material previously obtained by other workers employing different procedures.[102] Because of its insolubility in all solvents and of the negative results from x-ray examination, very little is known about this substance. Prolonged action of α-particles did give some hydrogen, but the indications were that it came from the solid polymer rather than from acetylene. The polymerization of acetylene was catalyzed by the presence of ions of inert gases, nitrogen and helium.[103] With ethylene the reactions were much more complicated, resulting in the formation of a liquid condensate and of gaseous methane, hydrogen and ethane.

The elimination of both hydrogen and methane and the formation of liquid products from unsaturated hydrocarbons by the action of α-particles was noted also by Heisig.[104] The hydrocarbons investigated were allene ($H_2C{=}C{=}CH_2$), allylene ($CH_3C{\equiv}CH$), dimethylacetylene ($CH_3C{\equiv}CCH_3$), 2-butene ($CH_3CH{=}CHCH_3$) and isoprene ($H_2C{=}CH{-}C(CH_3){=}CH_2$). From allene and allylene, however, the liquids were further changed into solids, this transformation occurring sooner with allylene. A heavy, viscous, rubbery mass was obtained from isoprene. In continuing this study,[105] it was further noted that propylene condensed to a light mobile liquid and slightly less hydrogen and methane were given off than from ethylene under similar conditions. Vinylacetylene, on the other hand, yielded a white solid (which became orange-colored on exposure to the action of α-particles) but practically no hydrogen or methane was evolved. Propylene and cyclopropane may also be polymerized, according to Heisig.

Methane, ethane, propane and butane undergo decomposition with the liberation of hydrogen when subjected to high speed electrons emitted from a Slach-

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[99] *Bull soc. chim. Belg.*, 1925, **34**, 119; *Chem. Abs.*, 1925, **19**, 1986.

[100] Lind and Bardwell, *J.A.C.S.*, 1926, **48**, 2335.

[101] Lind, Bardwell and Perry, *J.A.C.S.*, 1926, **48**, 1556.

[102] For example by Sabatier and Senderens (*Compt. rend.*, 1900, **130**, 250) on passing acetylene over copper at 200°-250° C. and by Berthelot and Gaudechon (*loc. cit.*) by the action of ultraviolet light on acetylene.

[103] Lind and Bardwell, *J.A.C.S.*, 1926, **48**, 1575.

[104] *J.A.C.S.*, 1931, **53**, 3245.

[105] Heisig, *J.A.C.S.*, 1931, **53**, 4460; *ibid.*, 1932, **54**, 2328.

Leonard cathode-ray tube.[106] The number of hydrogen molecules was about ten times the number of electrons corresponding with the filament current. On the assumption that only one per cent of the electrons actually entered the reaction vessel, it was calculated that the number of ion pairs produced in the gas was of the same order of magnitude as the number of molecules reacting.

The effect of cathode-ray bombardment of hydrocarbons has been extended by Schoepfle and Fellows[107] to include many different types of these substances. Saturated hydrocarbons, both paraffinic and cyclic, yielded large quantities of gas, containing both hydrogen and methane. With increasing molecular weight, the quantity of gas as well as its methane content became less and the hydrogen content increased. For the same molecular weight, hydrocarbons possessing branched chain structures gave larger proportions of gas. Olefins, both open chain and cyclic, reacted in a similar manner, but the volume of gas evolved was less than from the corresponding saturated compounds. Aromatics gave very little gas, the amount becoming appreciable only from those having a number of side chains or fairly long ones, e.g., hexamethylbenzene or p-cymene. The action of these rays on petroleum oils, and waxes, also results in the formation of hydrogen and methane and other saturated gaseous hydrocarbons.[108] While the rate as well as the quantity of gases evolved depended to a large extent upon the source and degree of refinement, in general those petroleum products having the larger proportion of saturated hydrocarbons yielded more gas than those containing a high percentage of unsaturated hydrocarbons.

McLennan and Patrick[109] observed that ethylene, subjected to cathode rays, was converted to a liquid, which on continued bombardment gave hydrogen, acetylene and saturated hydrocarbons. The polymerization of acetylene to a solid material by β-rays from radium is described by Mund and Jungers.[110] When methane, ethane, ethylene, or acetylene is exposed to β-rays from radium emanation in a differential manometer, a change in volume is noted, which is probably due to polymerization, according to Mund and Koch.[111] Ethane and ethylene produce minute drops of a highly refractive liquid. From acetylene is obtained a voluminous brownish-yellow amorphous powder, each pair of ions causing the union of 26 molecules of acetylene. A method for refining hydrocarbons is based upon the action of α-, β-, x-, ultraviolet or infra-red rays.[112]

The synthesis of liquid hydrocarbons from gaseous carbon compounds (e.g., coke-oven gas, natural gas or cracking gas) by the action of rapidly moving electrons (β-rays), or the combined action of β- and x-rays, is suggested by Plauson.[113] The reaction may be assisted by rotating electric or electromagnetic fields and by a catalyst suspended in the reacting gases. In addition to hydrocarbons, ketones and alcohols are obtained if the gases contain water vapor.

Stewart and Olson[114] studied the decomposition of hydrocarbons by positive rays. They concluded that the decomposition is due to dissociation by the ionizing electrons or to the secondary reaction between ions and neutral molecules. Selective absorption of hydrocarbon ions by propane and butane was observed. Natural H-rays have been produced by Pavlovski[115] from the action of α-rays on paraffin.

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[106] Lind, Marks and Glockler, *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 33; *Brit. Chem. Abs.* **A**, 1931, 578.

[107] *Ind. Eng. Chem.*, 1931, **23**, 1396.

[108] Schoepfle and Connell, *Ind. Eng. Chem.*, 1929, 21, 529.

[109] *Canadian J. Research*, 1931, **5**, 470; *Brit. Chem. Abs.* **A**, 1931, 1379.

[110] *Bull. soc. chim. Belg.*, 1931, **40**, 158; *Chem. Abs.*, 1931, **25**, 5084.

[111] *Bull. soc. chim. Belg.*, 1925, **34**, 119; *Brit. Chem. Abs.* **B**, 1925, 377.

[112] Schaeffer, French Patent 735,046, 1931; assigned to Compagnie téchnique des pétroles; *Chem. Abs.*, 1933, **27**, 1158.

[113] British Patent 309,002, 1927; *Chem. Abs.*, 1930, **24**, 299.

[114] *J.A.C.S.*, 1931, **53**, 1236.

[115] *Ann. phys.*, 1931, (10) **16**, 150.

The decomposition of a large number of hydrocarbons in the glow discharge has been reported by Linder and Davis,[116] who observed that the rate of gas evolution per unit of current increased with molecular weight. Furthermore, the proportion of insoluble residue increased with increasing ratio of carbon to hydrogen in the original hydrocarbon. Linder[117] also concluded, from experiments with n-decane vapor, that electrical conduction in gases may follow an electrochemical equivalency law similar to Faraday's law of electrolytic conduction in liquids, as the amount of reaction was found to be proportional to the current and independent of the voltage and vapor pressure.

The synthesis of acetylene from methane, or from a hydrocarbon mixture containing ethane, by direct-current glow discharges between unequally curved electrodes has been proposed.[118] The electrodes are arranged in a reaction chamber so that the cathode-fall space is approximately equal to the space between the electrodes. Hydrogen may be added to the reacting hydrocarbons. In the absence of hydrogen, diacetylene is one of the reaction products.

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[116] *J. Phys. Chem.*, 1931, **35**, 3649; *Chem. Abs.*, 1932, **26**, 1191.
[117] *Phys. Rev.*, 1930, **36**, 1375; *Chem. Abs.*, 1931, **25**, 3570.
[118] Inst. f. physikal. Grundlagen der Medizin, British Patent 357,534, 1930; *Brit. Chem. Abs.* **B**, 1931, 1105; French Patent 740,062, 1932; *Chem. Abs.*, 1933, **27**, 2101.

Chapter 10

Reactions of Hydrocarbons with Steam, Carbon Dioxide, and Ammonia

REACTIONS OF HYDROCARBONS WITH STEAM

When hydrocarbons are allowed to react with steam at high temperatures in the presence of catalysts they are transformed into hydrogen and oxides of carbon. The reactions of methane, the most resistant of the hydrocarbons, can be expressed by the following reversible equations:[1]

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

These reactions are strictly reversible, the equilibrium depending upon temperature and pressure conditions. The reaction of methane and steam at high temperatures is the reverse of the methane synthesis (reduction of the oxides of carbon by hydrogen) of Sabatier and Senderens[2] which takes place at lower temperatures.

The reactions of the higher hydrocarbons may be conceived to occur by initial decomposition at high temperatures into carbon, hydrogen, and methane, followed by reaction of carbon and methane with steam according to the equations:

$$C + H_2O \longrightarrow CO + H_2$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

Whatever the mechanism of the process, the reactions of ethane, propane and other paraffin hydrocarbons with steam may be summarized in the equations:

$$C_2H_6 + 2H_2O \rightleftharpoons 2CO + 5H_2$$
$$C_3H_8 + 3H_2O \rightleftharpoons 3CO + 7H_2$$
$$\text{or, in general, } C_nH_{2n+2} + nH_2O \rightleftharpoons nCO + (2n + 1)H_2.$$

Some of these processes are also reversible and it is actually possible to synthesize higher hydrocarbons by reduction of carbon monoxide with hydrogen in the presence of certain catalysts in the neighborhood of 300° C.[3]

From an industrial point of view the chief interest of these reactions lies in the possibility of producing hydrogen from gaseous hydrocarbons, more particularly from methane, by its reaction with steam.[4] By this process considerably more hydrogen can be produced from a given quantity of methane, or hydrocarbon gas, than by purely thermal decomposition processes (described in Chapter 7). Thus, by thermal decomposition according to the equation, $CH_4 \rightarrow C + 2H_2$, one volume of methane ultimately gives two volumes of hydrogen, but by reaction with steam at high temperatures one volume of methane yields three volumes of hydrogen.[5]

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[1] Stanley and Nash, *J.S.C.I.*, 1929, **48**, 1T. See also I. G. Farbenindustrie A.-G., British Patent 347,802, 1930; *Chem. Abs.*, 1932, **26**, 2893.

[2] *Compt. rend.*, 1902, **134**, 514; *Chem. Soc. Abs.*, 1902, **82** (1), 333. See also *Compt. rend.*, 1902, **134**, 689; *Chem. Soc. Abs.*, 1902, **82** (2), 317.

[3] See, for example, Fischer and Tropsch, *Brennstoff-Chem.*, 1923, **4**, 193; *Chem. Abs.*, 1924, **18**, 349. Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930, 674.

[4] Attempts to produce methyl alcohol from methane and steam according to the reaction $CH_4 + H_2O \rightarrow CH_3OH + H_2$ have not met with much success. However, Dreyfus (British Patent 337,410, 1929; *Brit. Chem. Abs.* **B**, 1931, 194) reported obtaining methyl and other alcohols from methane and steam heated at 200° to 500° C. at 50 to 100 atmospheres pressure in the presence of catalysts such as potassium dichromate and zinc oxide, zinc chromate with cobalt oxide, or zinc chromate.

Lang[6] was one of the first to investigate the reaction between methane and steam, his apparatus consisting of a porcelain tube filled with lumps of porcelain and heated to a high temperature.[7] An excess of steam was used with methane and yielded oxides of carbon and hydrogen. Because of the inactivity of his contact materials, Lang obtained yields of the oxides of carbon not exceeding 10 per cent of the theoretical.

Mayer and Altmayer[8] calculated the proportions of the reactants in the equilibria,

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

and

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

by Haber's[9] method. Tables 64 and 65 show their calculated equilibrium constants and concentrations for different temperatures at one atmosphere pressure:

TABLE 64.—*Equilibrium:* $CH_4 + H_2O \rightleftharpoons CO + 3H_2$.

Temp. ° Absolute	K_1	CO	H_2	CH_4	H_2O
		Per Cent			
700	0.000082	2.79	8.37	44.43	44.43
800	0.0104	8.13	24.39	33.73	33.73
900	0.4845	15.74	47.22	18.51	18.51
1000	11.14	21.42	64.26	7.17	7.17
1100	153.8	23.81	71.43	2.38	2.38

TABLE 65.—*Equilibrium:* $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$.

Temp. ° Absolute	K_2	CO_2	H_2	CH_4	H_2O
		Per Cent			
600	0.00000592	1.9	7.6	30.16	60.32
700	0.001023	4.89	19.56	25.19	50.38
800	0.0539	8.84	35.36	18.60	37.20
900	1.287	12.84	51.36	11.92	23.84
1000	17.66	15.75	63.00	7.08	14.16
1100	159.2	17.55	70.20	4.08	8.16

In Tables 64 and 65

$$K_1 = \frac{p_{CO} \times p^3_{H_2}}{p_{CH_4} \times p_{H_2O}}$$

and

$$K_2 = \frac{p_{CO_2} \times p^4_{H_2}}{p_{CH_4} \times p^2_{H_2O}}$$

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[5] Dominick (*Przemysl Chem.*, 1925, 9, 1; *Chem. Abs.*, 1926, 20, 2229) discussed these points in considering the methods of producing cheap hydrogen from natural gas. See also Karzhavin, *J. Chem. Ind.*, Moscow, 1932, No. 6, 24; *Chem. Abs.*, 1932, 26, 5399.

[6] *Z. phys. Chem.*, 1888, 2, 161; *Chem. Soc. Abs.*, 1888, 54, 1029.

[7] The use of lime as a contact agent for the decomposition of naphtha by steam had been suggested as early as 1880. (Stern, British Patent 2,787, 1880; see Taylor, "Industrial Hydrogen," Chemical Catalog Co., Inc., New York, 1921, 158; and Green, "Industrial Catalysis," Macmillan Co., New York, 1928, 370.)

[8] *J. Gasbel.*, 1909, 52, 326; see also, Mayer, Henseling, Altmayer and Jacoby, *J. Gasbel.*, 1909, 52, 166, 194, 238, 282, 305; *Chem. Soc. Abs.*, 1909, 96 (1), 753.

[9] Haber, "Thermodynamik technischer Gasreaktionen," Munich, 1905. Translated by Lamb, Longmans, Green & Co., New York, 1908.

Neumann and Jacob[10] investigated these equilibria both practically and theoretically. Their main conclusions are in good agreement with those of Mayer and Altmayer and their practical results from methane and steam may now be considered in some detail. Using a nickel-magnesium oxide catalyst (6.6 grams of nickel and 45.0 grams of magnesium oxide) and a gas mixture of 43 per cent methane and 57 per cent steam the results in Table 66 were obtained. The gas rate in all runs was 5 cc. per minute.

TABLE 66.—*Reaction of 43% Methane and 57% Steam.*

	Analysis of Resulting Gas			
Temp. ° C.	CH_4	CO	CO_2	H_2
	Per Cent			
330	100.0	—	—	—
470	75.5	2.0	2.6	19.9
544	48.1	4.1	3.9	43.9
600	29.7	4.6	5.1	60.6
700	11.5	15.0	2.7	70.8
860	2.0	23.4	—	74.6
940	0.9	24.3	—	74.8
980	0.6	24.7	—	74.7
1034	0.3	24.8	—	74.9

The effect of an excess of steam was investigated and it was found that a gas mixture containing 22.5 per cent methane, 22.5 per cent nitrogen and 55 per cent steam was recomposed to the extent indicated in Table 67.

TABLE 67.—*Reaction of 22.5% Methane and 55% Steam (diluted with nitrogen).*

	Analysis of Resulting Gas				
Temp. ° C.	CH_4	CO	CO_2	H_2	N_2
	Per Cent				
320	50.0	—	—	—	50.0
616	18.9	3.7	3.6	35.6	38.2
830	1.5	16.1	1.2	53.5	27.7
1040	0.1	19.4	0.4	58.8	21.3

Neumann and Jacob concluded that at moderate temperatures (about 600° C.) both reactions tend to occur simultaneously. At high temperatures the reaction producing carbon monoxide predominates probably because of the decomposition of the carbon dioxide formed by the other reaction:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

Even with an excess of steam at very high temperatures the composition of the resulting gases may be expressed by the equation:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

The experimental results of Neumann and Jacob for this reaction are in good agreement with the values calculated from the following equation, deduced from free energy data:

$$\log K_p = \frac{-10308}{T} + 4.87 \log T + 0.000066\,T - 0.000000081\,T^2 - 3.04$$

$$\text{where } K_p = \frac{p_{CO} \times p^3_{H_2}}{p_{CH_4} \times p_{H_2O}}$$

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[10] *Z. Elektrochem.*, 1924, 30, 557; *Chem. Soc. Abs.*, 1925, 128 (2), 532.

Pease and Chesebro[11] determined the equilibrium constant of the reaction $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$ at temperatures of about 500° C. Equilibrium was approached from both directions. At 505° C. the value of the constant was found to be 0.037 (the partial pressures of the reactants and products being expressed in atmospheres). These investigators also pointed out that two other reactions,

$$\begin{aligned} CH_4 + H_2O &\longrightarrow CO + 3H_2 \\ \text{and } CO_2 + H_2 &\longrightarrow CO + H_2O \end{aligned}$$

must be taken into account at higher temperatures.

The equilibrium constant, K_p, of the reaction

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

may also be calculated from the following equation, deduced by Lewis and Randall[12] from free energy data:

$$\log K_p = \frac{-8100}{T} + 3.96 \log T + 0.00104\,T - 0.00000023\,T^2 - 3.15$$

$$\text{in which } K_p = \frac{p_{CO_2} \times p^4{}_{H_2O}}{p_{CH_4} \times p^2{}_{H_2O}}$$

The catalytic conversion of methane to hydrogen and oxides of carbon has been investigated by Gluud and his collaborators,[13] who found that the conversion takes place satisfactorily in the presence of a nickel catalyst supported on special refractory materials which, unlike many other materials tried, do not promote the formation of soot. In applying the process to gases containing sulphur, it was observed that the nickel catalyst is gradually poisoned by the formation of nickel sulphide but that its activity can be restored by oxidation with steam. Soot formation, which is likely to occur during the preheating of the methane, was avoided by rapid heating of the gases following the addition of small proportions of air. The observation that the activity of the catalyst is seriously reduced by the presence of sulphur compounds conflicts with the results of Fischer and Tropsch.[14] They investigated the reactions of methane with both steam and carbon dioxide in the temperature range 840° to 920° C. in a small externally heated laboratory reaction tube in the presence of a number of catalysts. These investigators found that the best catalysts, consisting of nickel or cobalt promoted with alumina and supported on refractory materials, are not seriously injured by the presence of sulphur compounds in the gas used. Though the initial conversions were higher than those obtained after the catalyst had been in use for some time, the loss of activity soon ceased and was succeeded by an apparently indefinite period of constant activity. Goodfellow and Spencer[14a] observed that chromium catalysts are activated by adding about 1 per cent of hydrogen sulphide (or other gaseous sulphur compounds) to the reacting gases.

A cyclic process for catalytically converting methane, or gases containing methane, into carbon monoxide and hydrogen by reaction with steam has been described by Hawk, Golden, Storch and Fieldner.[15] The catalysts used in this work were prepared by depositing the nitrates of nickel, cobalt or aluminum, or nickel and aluminum, on small pieces of porous refractory material, heating the nitrates for several hours at 250° to 300° C. to convert them to the oxides, and finally reducing the oxides by heating first slowly to 700° C. and then rapidly to 1060° to 1150° C. in the presence of a mixture of natural gas and insufficient air for complete combustion. Of the catalysts so prepared the nickel catalyst was found to be the most effective; the nickel-aluminum [15a] and cobalt catalysts were unsatisfactory.

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[11] *J.A.C.S.*, 1928, **50**, 1464.

[12] "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York. 1923. 485, 571, 576.

[13] Gluud, Keller, Klempt, Bestehorn, Brodkorb, Schröter and Curland, *Ber. Ges. Kohlentech.*, 1930, **3**, 211-370; *Chem. Abs.*, 1931, **25**, 2269.

[14] *Brennstoff-Chem.*, 1928, **9**, 39; *Chem. Abs.*, 1928, **22**, 2652.

[14a] British Patent 370,457, 1932; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, **27**, 3787.

[15] *Ind. Eng. Chem.*, 1932, **24**, 23.

The optimum temperatures for the reaction were from 900° C. to 1000° C., and in this range almost theoretical conversion was obtained. As the ratio of steam to methane was increased, however, larger quantities of carbon dioxide were obtained without decreasing the percentage of methane converted.

These investigators also calculated the free energy and equilibrium constants for the reaction between methane and steam from the data of Eastman [16] and Storch.[17] The values are given in Table 68.

TABLE 68.—*Free Energy and Equilibrium Constants for Reaction between Methane and Steam.*

T ° Absolute	1073	1173	1273
ΔF	—10,700	—16,722	—22,735
K_p	150.5	1296	7940

$$\Delta F \text{ represents the free energy and } K_p = \frac{p_{CO} \times p^3_{H_2}}{p_{CH_4} \times p_{H_2O}}$$

Almost complete reaction between methane and steam at temperatures of 850° C. in the presence of reduced nickel oxide was obtained by Klyukvin and Klyukvina.[18] The reaction, however, was retarded by the addition of aluminum oxide to the nickel catalyst. Activated vegetable carbon gave 100 per cent conversion of the methane, although the primary reaction was accompanied by another reaction, namely that between carbon and steam:

$$C + 2H_2O \rightleftharpoons CO_2 + 2H_2$$

The same catalysts could be used for the reaction between methane and carbon dioxide.

According to Kubota and Yamanaka [19] certain metallic oxides (alumina, zirconia, thoria, beryllia, chromium oxide, ferric oxide, ceria, or magnesia) activate a nickel catalyst in decomposing methane by steam at about 1000° C. The activation effects of these oxides are very marked with a ratio of 100 atoms of nickel to 1 molecule of the added oxide. Alumina gives a large proportion of carbon dioxide, and magnesia, a large proportion of carbon monoxide. In the presence of a nickel-aluminum oxide-potassium carbonate catalyst, methane was rapidly and completely decomposed by steam into hydrogen and carbon dioxide at 650° C.[19a]

A study of catalysts for producing hydrogen from natural gas and water vapor has been made by Patryn and Ziolkowski.[20] Reduced iron, nickel, and cobalt deposited on asbestos, oxides of these metals, and mixtures of these reduced metals were tried. Their work can be summarized as follows: Best hydrogen yields are obtained with reduced nickel at 350° to 550° C. with 1 volume of methane to 10 volumes of water vapor. Iron and cobalt are immediately oxidized on contact with water vapor. The oxides of these metals act as catalysts only at temperatures above 800° C. Mixtures of nickel, iron and cobalt were found to be poorer catalysts than nickel alone. Of the three, nickel is the most resistant to oxidation by water vapor. This resistance can be raised by the addition of a difficultly reducible oxide (oxide of aluminum, manganese, chromium, zinc or potassium). A mixture of 20 per cent alumina and 80 per cent of reduced nickel gave the best results with 5 volumes of water vapor and 1 volume of methane. A gas mixture, typical of that obtained with a nickel catalyst in this process, is given in Column I of the table below. Column II gives the composition of the same gas after being washed with alkali. Column III shows the result obtained by processing the mixture a second time.

[15a] *Cf.* Fujimota, *J. Soc. Chem. Ind. Japan,* 1933, 36, 147B; *Brit. Chem. Abs.* A, 1933, 790.

[16] *U. S. Bur. Mines, Information Circ.* 6125 (1929).

[17] *J.A.C.S.,* 1931, 53, 1266.

[18] *J. Chem. Ind. Russia,* 1930, 7, 743, 877; *Brit. Chem. Abs.* A, 1931, 1377. *Prirodnuie Gazui,* 1931, 2, 91; *Chem. Abs.,* 1932, 26, 1416.

[19] *Bull. Chem. Soc. Japan,* 1929, 4, 211; *Chem. Abs.,* 1930, 24, 822; *Brit. Chem. Abs.* A, 1930, 43.

[19a] Takenaka, *J. Fuel Soc. Japan,* 1933, 12, 57; *Chem. Abs.,* 1933, 27, 3585.

[20] *Przemysl Naftowy,* 1932, 7, 206, 224; *Chem. Abs.,* 1932, 26, 5731.

	I	II	III
		Per Cent	
Carbon dioxide	15.5	0.3	6.8
Carbon monoxide	5.5	6.1	3.0
Hydrogen	74.0	87.6	88.4
Methane	5.0	6.0	1.8

REACTIONS OF HYDROCARBONS WITH CARBON DIOXIDE

Hydrocarbons react with carbon dioxide at high temperatures in the presence of catalysts to yield mixtures of carbon monoxide and hydrogen.[21] The reaction of methane, which was observed in 1888 by Lang,[22] can be represented by the equation:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

Mayer and Altmayer [23] calculated the equilibrium concentrations of these reactants at different temperatures under 1 atmosphere pressure, using Haber's method, with the results in Table 69.

TABLE 69.—*Equilibrium:* $CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2$.

Temp. ° Absolute	CO	H_2	CO_2	CH_4
	Per Cent			
700	3.44	3.44	46.56	46.56
800	12.83	12.83	37.17	37.17
900	29.44	29.44	20.56	20.56
1000	43.06	43.06	6.94	6.94
1100	48.10	48.10	1.90	1.90

Fischer and Tropsch [24] investigated the effects of various catalysts on this reaction. The best catalyst was found to be nickel with alumina as a promoter supported on clay fragments. Cobalt proved as active as nickel and its activity is increased by the presence of alumina. Copper, iron and molybdenum were not active as catalysts.

[21] The possibility of producing alcohols, aldehydes, ketones, acids and esters by the reaction of carbon dioxide and hydrocarbons is discussed in Chapter 42.

[22] *Z. physik. Chem.*, 1888, **2**, 161; *Chem. Soc. Abs.*, 1888, **54**, 1029. Berthelot (*Bull. soc. chim.*, 1870, (2) **13**, 9; *Chem. Zentr.*, 1870, 216) attempted to produce a reaction between methane (as well as ethane) and carbon dioxide in sunlight and in sealed tubes at 100° and 200° C. for 20 hours. No changes were observed.

[23] *J. Gasbel.*, 1909, **52**, 326; *Chem. Soc. Abs.*, 1909, **96** (1), 753.

[24] *Brennstoff-Chem.*, 1928, **9**, 39; *Chem. Abs.*, 1928, **22**, 2652.

Klyukvin and Klyukvina[25] recorded experiments in which an equimolecular mixture of carbon dioxide and methane was passed at 1000° C. with a time of contact of approximately 38 seconds (I) through an empty porcelain tube, (II) through an empty iron tube, and (III) over a reduced nickel catalyst. The conversions of methane into carbon monoxide and hydrogen were (I) 43 per cent, (II) 58 per cent, and (III) 97.6 per cent, respectively. With an active nickel catalyst (III), the gaseous reaction products consisted of 47 per cent of carbon monoxide, 48.6 per cent of hydrogen, 2.6 per cent of nitrogen, and no by-products.

Fischer and Pichler[26] studied the carbon dioxide-methane reaction in the presence of a nickel catalyst at various temperatures under atmospheric and subatmospheric pressures. Reduction of pressure below atmospheric is so favorable to this reaction (as might be expected from theoretical considerations) that complete conversion could be effected at 500° to 600° C. under 0.01 atmosphere pressure, whereas a temperature of 900° C. was required to secure the same result at 1 atmosphere.[27] At lower pressures the reaction could be carried almost to completion at even lower temperatures. The reaction velocity increased in inverse ratio to the pressure.

Peters and Pranschke[28] showed that the reaction between methane and steam, or methane and carbon dioxide, can be carried almost to completion by subjecting the gas mixture at high rates of flow to a high-voltage electric discharge at pressures below atmospheric. The optimum voltage is 5000 to 6000 volts. At lower voltages a considerable part of the methane is converted into acetylene.

Hawk, Golden, Storch and Fieldner[29] pointed out that between 800° and 1000° C. the reaction between methane and carbon dioxide proceeds to approximately the same extent as that between methane and steam. The free energy and equilibrium constants for the first, as calculated by these workers, are:

TABLE 70.—*Free Energy and Equilibrium Constants for Reaction between Methane and Carbon Dioxide.*

$T°$ Absolute	1073	1173	1273
ΔF	−11,251	−18,112	−24,943
K_p	194.8	2,353	18,990

where ΔF represents free energy, and $K_p = \dfrac{p^2_{CO} \times p^2_{H_2}}{p_{CH_4} \times p_{CO_2}}$

The change of equilibrium with temperature in the reaction between methane and carbon dioxide can be deduced from free energy data and is represented by the equation:

$$\log K_p = \frac{-12450}{T} + 7.59 \log T - 0.00236\,T + 0.000000068\,T^2 - 6.64$$

where $K_p = \dfrac{p^2_{CO} \times p^2_{H_2}}{p_{CH_4} \times p_{CO_2}}$

Later, Storch and Golden[29a] observed that, at 1500° C. and a time of contact of 0.03 to 0.04 second, a mixture of methane (25 per cent) and carbon dioxide

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[25] *J. Chem. Ind. Russia*, 1930, 7, 743; *Brit. Chem. Abs.* A, 1931, 1377.

[26] *Brennstoff-Chem.*, 1931, 12, 365; *Chem. Abs.*, 1931, 25, 5970.

[27] Karzhavin (*J. Chem. Ind., Moscow*, 1932, No. 6, 24; *Chem. Abs.*, 1932, 26, 5399) attained most efficient conversion with a ratio of methane to steam of 1:2 at 900° C. and 1 atmosphere pressure.

[28] *Brennstoff-Chem.*, 1930, 11, 473; *Chem. Abs.*, 1931, 25, 645; *Ges. Abhandl. Kenntnis Kohle*, 1930, 10, 271.

[29] *Ind. Eng. Chem.*, 1932, 24, 23.

[29a] *Ind. Eng. Chem.*, 1933, 25, 768.

(75 per cent) yielded about 10 per cent of unsaturated hydrocarbons (principally acetylene), 10 per cent carbon monoxide, 35 per cent hydrogen and 45 per cent unchanged methane. With somewhat longer times of contact the percentage of hydrogen and carbon monoxide increased, the percentage of unsaturated hydrocarbons remaining approximately constant. At this high temperature steam was less desirable as a diluent than carbon dioxide because of the loss of methane as carbon which deposited in the reaction tube. With carbon dioxide this loss amounted to only a few per cent, though with steam it increased to 15 to 20 per cent.

Schmidt and Neumann[30] studied the equilibrium constants of this reaction at temperatures from 500° to 800° C. using nickel supported on silica gel. They found an agreement between the observed methane transformation and that calculated from free-energy data at temperatures above 600° C. Below 600° C., however, the methane converted was greater than that deduced from the free-energy data. This difference is attributed to two side-reactions:

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

followed by

$$H_2O + CH_4 \longrightarrow CO + 3H_2$$

Industrial Applications of the Reactions of Steam and Carbon Dioxide with Hydrocarbons

From the above review of the catalytic reaction of methane with steam, it is clear that hydrogen may be produced in accordance with the following two equations:

$$(1)\ CH_4 + H_2O \longrightarrow CO + 3H_2 - 48.9 \text{ kg. cals.}$$

$$(2)\ CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 - 38.5 \text{ kg. cals.}$$

Since the first reaction produces 3 volumes of hydrogen, and the second 4 volumes of hydrogen, per unit volume of methane reacting, it is evident that these are superior to the purely thermal decomposition of methane for hydrogen production. Moreover, both reactions can be efficiently catalyzed. The catalysts have a long life and can be easily revivified.

Of these reactions, the first, which produces a mixture of carbon monoxide and hydrogen in the molar ratio of 1:3, can be carried almost to completion at sufficiently high temperatures (over 900° C.). The resulting mixture of carbon monoxide and hydrocarbon can be utilized, after an adjustment of the proportions of these two gases, in the synthesis of methanol. On the other hand, where the production of pure hydrogen is desired, it is advantageous to subject the gas mixture to a further reaction with steam (at a lower temperature (500° C.) in the presence of a catalyst) to convert carbon monoxide into carbon dioxide according to the well-known water-gas equilibrium:[31]

$$(3)\ CO + H_2O \rightleftharpoons CO_2 + H_2$$

By conducting the steam reaction in these two stages, one volume of methane yields a mixture of 4 volumes of hydrogen and 1 volume of carbon dioxide, from which the latter can be easily eliminated either by absorption in an alkaline liquid or by washing with water under pressure.

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[30] *Z. Elektrochem.*, 1932, **38**, 925; *Chem. Abs.*, 1933, **27**, 1260.

[31] The water-gas reaction can be successfully operated to yield a gas containing only small proportions of carbon dioxide by using excess of steam at about 530° C. in the presence of catalysts, such as iron-alumina, (Evans and Newton, *Ind. Eng. Chem.*, 1926, **18**, 513), dolomite (Gluud, *Ber. Ges. Kohlentechnik*, 1930, **3**, 211; Klempt and Brodkorb, *ibid.*, 1930, **3**, 261), and other catalysts (see Taylor, "Industrial Hydrogen," Chemical Catalog Co., Inc., New York, 1921, 158). See also Chapter 7.

A similar result is obtained by carrying out the methane-steam reaction according to equation (2) (see above). Unfortunately, it is impossible to conduct this reaction in such a way as to obviate the simultaneous occurrence of the reaction of equation (1), which produces carbon monoxide. By operating at temperatures of the order of 500° to 600° C. with sufficiently active catalysts and an excess of steam, reaction (2) can be made the preponderant one. The proportion of steam required to suppress the carbon monoxide reaction to desired limits is high, and difficulties are likely to be encountered through poisoning of the catalysts by carbon deposition and because of the necessity of using much longer time of contact.[32] As the reaction temperature is raised the equilibrium is shifted more and more to favor carbon monoxide production and the reaction of equation (1) becomes increasingly important even in the presence of excess steam. It has been found that the relative amounts of carbon monoxide and carbon dioxide formed at various reaction temperatures and steam ratios are in good agreement with those demanded by the water-gas equilibrium. These considerations lead to the belief that probably the best method of utilizing the steam-methane reaction for the production of hydrogen is in a two-stage process involving first the catalytic reaction at high temperature according to equation (1), followed by further treatment with steam at lower temperatures in the presence of a catalyst for the water-gas reaction. This yields ultimately a gas mixture containing about 20 per cent carbon dioxide and 80 per cent hydrogen with only traces of methane and carbon monoxide.

In carrying out the reaction of methane with steam at high temperatures to yield hydrogen and carbon monoxide, catalysts of nickel supported on inert refractory material appear to be best. Evidence regarding the life of such catalysts is somewhat conflicting but it appears that sulphur compounds in the gas are likely to cause a decline in activity. According to Neumann and Jacob,[33] the deposition of free carbon on the catalyst is likely to occur under certain circumstances, particularly when the gases contain appreciable proportions of homologues of methane. Deposition of free carbon causes rapid deterioration of the catalyst and necessitates frequent revivification. To minimize this, an excess of steam would seem advantageous. However, Hawk, Golden, Storch and Fieldner [34] observed that an increase in the steam concentration in the reacting gases promotes the formation of more carbon dioxide at the expense of carbon monoxide without increasing the fraction of methane converted.

Perhaps the main technical difficulty associated with the application of this reaction is the highly endothermic nature of the process,

$$CH_4 + H_2O \longrightarrow CO + 3H_2 - 48.9 \text{ kg. cals.},$$

combined with the high temperature necessary for complete reaction. The difficulties involved in the external heating of large catalytic units, into which much heat energy must be introduced at a high temperature level, are very great. This difficulty has been overcome in some processes [35] by applying internal heating to the reacting system through the exothermic oxidation of methane according to the equation:

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[32] Hirsch (*Bull. Mem. Soc. Ing. Civ. France*, 1932, 85, 286; *Brit. Chem. Abs.* B, 1932, 919) has also studied these conditions which influence the conversion of natural and coke-oven gas into hydrogen.

[33] *Z. Elektrochem.*, 1924, 30, 557; *Chem. Soc. Abs.*, 1925, 128 (2), 532.

[34] *Loc. cit.*

[35] See, for example, Pictet, British Patent 24,256, 1910; *J.S.C.I.*, 1911, 30, 1044.

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2 + 7{,}000 \text{ cals.}$$

To accomplish this, a mixture of methane, steam and oxygen is passed through the catalyst chamber. Unless high proportions of oxygen are employed, however, the exothermic oxidation reaction will not provide sufficient heat to counterbalance the endothermic methane-steam reaction and, in general, it will be necessary to apply external heat to the reaction chamber in addition. If air is used instead of oxygen, the resulting gas will contain nitrogen and, by adjustment of the proportions of the constituents, a mixture suitable for the ammonia synthesis may be obtained.

According to Hawk, Golden, Storch and Fieldner, the use of air or oxygen in the reacting system often introduces another difficulty. Certain activated nickel catalysts are poisoned by oxygen, probably on account of the formation of a protective film of oxide, but apparently this difficulty was not experienced by these investigators, who supplied the heat of reaction directly by alternately blasting the catalyst bed with a gas-air mixture and introducing the methane-steam mixture. It was found possible to prepare catalysts which were uninjured by this treatment even when burned with a moderate excess of oxygen on the catalytic surface.

Instead of effecting the reaction of the mixture of methane, steam and air (or oxygen) in a single step in the presence of the catalyst, the process may be operated in two stages. In the first of these the exothermic oxidation reaction is utilized to heat the gaseous mixture and in a second stage the methane-steam reaction is allowed to proceed in the presence of the catalyst. This method avoids poisoning of the catalyst by free oxygen.

In another process[36] steam and methane are passed through progressively hotter zones to complete reaction and the products are passed into progressively cooler zones where air or a mixture of air and oxygen is added to oxidize carbon monoxide to carbon dioxide. A mixture of nitrogen and hydrogen is obtainable in this way which can be used after the separation of CO_2 for the synthesis of ammonia. Gases from the distillation or gasification of fuel may be passed with steam at 200° to 600° C. under pressure over such catalysts as ferrous oxide, nickel, bismuth, lead, or metals of the copper group.[37]

The methane-steam reaction is utilized for the production of hydrogen by the Standard Oil Company of New Jersey. A two-stage process is employed, in the first of which the reaction

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

is carried out in the presence of catalysts at about 870° C. (1600° F.). In this step cracking gases and steam are used. A further reaction with steam in the presence of a catalyst at 455° C. (850° F.) converts the carbon monoxide into carbon dioxide and yields more hydrogen. No technical details of the plant or of the operating conditions used have been published. The gaseous mixture leaving the final stage contains 79 per cent of hydrogen, 20 per cent of carbon dioxide, and 1 per cent of other gases. Carbon dioxide is removed, after compression to 240 pounds per square inch pressure, by washing with water and subsequently scrubbing in a bubble plate tower with aqueous triethanolamine to remove the last traces. The gas, containing over 97 per cent hydrogen, is compressed to 3600 pounds per square inch for use in the hydrogenation of oil.[38]

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[36] Hydro-Nitro S. A., French Patent 723,817, 1931; *Chem. Abs.*, 1932, **26**, 4823. British Patent 390.849, 1931; *Brit. Chem. Abs.* **B**, 1933, 534. See also I. G. Farbenindustrie A.-G., British Patent 364,106, 1930; *Brit. Chem. Abs.* **B**, 1932, 248.

[37] Hydro-Nitro S. A., French Patent 724,825, 1930; *Chem. Abs.*, 1932, **26**, 4922.

Gross[39] gasified fuels with a mixture of oxygen, air, and water vapor to convert the hydrocarbons into carbon monoxide and hydrogen. The air content can be adjusted to produce a gas mixture for conversion to ammonia.

Geisenberger[40] generated hydrogen mixed with carbon monoxide or dioxide by heating light hydrocarbons or other carbonaceous materials, such as bitumen, shale, beeswax, or turpentine, with steam in a retort. Rose[41] passed superheated steam and a hydrocarbon mixture through a refractory tube heated to 1200° C. to obtain a gaseous fuel.

Gluud and others[42] suggested a process of technical interest. In large-scale experiments using a mixture of methane, steam, and air to supply a mixture of nitrogen, carbon monoxide, and hydrogen, they showed that the process could be carried out satisfactorily in an externally heated converter. This was constructed of a heat-resisting alloy (20 per cent nickel, 25 per cent chromium, and 55 per cent iron).[43] The mixture of gas with regulated amounts of air and steam was passed upward through a cylindrical column (94 cm. long and 12 cm. in diameter) of catalyst consisting of nickel supported on a refractory carrier. The results obtained in this plant are exemplified by the treatment of a coal distillation gas containing 6 per cent carbon monoxide, 26 per cent methane, 55 per cent hydrogen, and 8 per cent nitrogen. Passing 6 cubic meters of this gas mixed with 3 kilograms of steam and 3 cubic meters of air per hour over the above volume of catalyst at about 1050° C. produced a gas mixture consisting of 2 per cent carbon dioxide, 17 per cent carbon monoxide, 56.5 per cent hydrogen, and 24.5 per cent nitrogen with only traces of methane.

Without air only about 3.5 cubic meters of coal distillation gas per hour could be converted into a methane-free product with this equipment. By introducing air into the reacting gas mixture at proper intervals in the catalyst bed, the methane content of the gaseous products could be reduced to 0.03 to 0.09 per cent. The gaseous products of this high-temperature treatment were subsequently subjected to further reaction with steam at lower temperatures in the presence of a catalyst for the water-gas reaction (dolomite) and practically all the carbon monoxide could thus be converted into carbon dioxide. The carbon monoxide content of the product could be reduced to about 0.05 to 0.07 per cent by volume.

The technical application of the reaction between methane and carbon dioxide,

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2,$$

is beset by the same difficulties encountered in the reaction between steam and methane at high temperatures. Both reactions can only be carried to completion at high temperatures (1000° C. and over) and both are highly endothermic. The methane-carbon dioxide reaction is catalyzed by the same catalysts effective in the methane-steam reaction.

[38] Byrne, Gohr, and Haslam, *Ind. Eng. Chem.*, 1932, 24, 1129; Reid, *Refiner*, 1932, 11, 449. See also Mockler, *Oil and Gas J.*, 1932, 31, No. 13, 10; *Chem. Abs.*, 1932, 26, 5742; Haslam and Russell, *Ind. Eng. Chem.*, 1930, 22, 1030.

[39] British Patent 289,080, 1928; *Brit. Chem. Abs.* **B**, 1929, 841.

[40] French Patent 361,492, 1905.

[41] U. S. Patent 1,252,033, Jan. 1, 1918; *Chem. Abs.*, 1918, 12, 760.

[42] Gluud, Keller, Klempt, Bestehorn, Brodkorb, Schröter and Curland, *Ber. Ges. Kohlentechnik*, 1930, 3, 211-370. *Cf.* Hirsch, *Bull. mem. soc. ing. civ. France*, 1932, 85, 286; *Brit. Chem. Abs.* **B**, 1932, 919.

[43] Keller and Klempt, *Ber. Ges. Kohlentechnik*, 1930, 3, 230; *Brit. Chem. Abs.* **B**, 1931, 325.

Pictet[44] suggested the decomposition of petroleum vapors in such a way that carbon, instead of being deposited, is converted into carbon monoxide by the action of steam. By admitting a regulated quantity of oxygen, so that the combination of the oxygen with the carbon provides all the heat required for the reaction, it is then only necessary to heat the hydrocarbons initially to their temperature of dissociation. Water and hydrocarbon alone, when fed into an iron tube about 3 to 4 meters long heated at 1350° C., yield hydrogen and carbon monoxide. However, if oxygen is added to the mixture the temperature of the tube may be reduced to 1200° C.[45] In generating hydrogen from hydrocarbons, Tyrer[46] added only a limited proportion of steam to the reacting mixture to render the process independent of external heat.

It has been proposed also to pass hydrocarbon gases through an apparatus consisting of non-combustible checker material heated to a temperature high enough to decompose the hydrocarbons, and simultaneously to introduce steam. In this manner reaction is effected and gas consisting essentially of hydrogen and carbon monoxide, in the ratio of 2:1 or 3:1, is obtained.[47]

Dieffenbach and Moldenhauer[48] have recommended a process for the production of hydrogen by the reaction of steam with hydrocarbons, or their oxygenated derivatives, at high temperatures. The mixture is heated to a moderate temperature, or kept in contact with the catalytic surface for such a short time that, simultaneously with hydrogen, only carbon dioxide is produced. From the resulting mixture of hydrogen and carbon dioxide the latter may be removed easily, leaving more or less pure hydrogen. As catalysts, wire gauzes of nickel, cobalt or platinum, disposed transversely to the direction of flow of the gases and heated electrically, are suggested.

Dibdin and Woltereck[49] obtained an illuminating and heating gas by passing a mixture of paraffin hydrocarbons and superheated steam over a porous spongy contact agent such as ferroso-ferric oxide.

Mittasch and Schneider[50] developed a process for the production of hydrogen by the interaction of hydrocarbons and steam in the presence of a nickel catalyst at temperatures of 800° to 1000° C. The nickel may be supported by refractory material (ignited magnesium oxide). Besides gases, liquid or solid hydrocarbons or gas mixtures containing hydrocarbons, such as coal gas, may be used. The nickel may be mixed with other metals or metallic oxides. The process may be carried out in such a manner that alternately hydrocarbon-air and hydrocarbon-steam mixtures are passed through the reaction chamber. The resulting gas mixture is subjected to the further action of steam at lower temperatures to convert the carbon monoxide into dioxide. In a related process[51] carbon dioxide is substituted, either partly or completely, for steam and the reaction carried out at 900° to 1100° C. Under such conditions natural gas containing 90 per cent of methane is rapidly converted into a mixture of hydrogen and carbon monoxide by reaction with 3 to 4 times its volume of carbon dioxide.[52]

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[44] French Patent 421,838, 1910; *J.S.C.I.*, 1911, **30**, 542; British Patent 24,256, 1910; *J.S.C.I.*, 1911, **30**, 1044.

[45] See also British Patent 13,397, 1911; *J.S.C.I.*, 1912, **31**, 641; and British Patents 14,703, 1911, and 16,373, 1911, additions to British Patent 13,397, 1911; *J.S.C.I.*, 1912, **31**, 686, 805.

[46] British Patent 323,864, 1928; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1930, **24**, 3331.

[47] Odell, U. S. Patent 1,841,201, Jan. 12, 1932; assigned to Columbia Engineering and Management Corp.; *Chem. Abs.*, 1932, **26**, 1758.

[48] German Patent 229,406, 1909; *J.S.C.I.*, 1911, **30**, 210.

[49] British Patent 26,666, 1905; *J.S.C.I.*, 1906, **25**, 1139. French Patent 371,192, 1906; *J.S.C.I.*, 1907, **26**, 249. See also Harter, U. S. Patent, 1,920,858, Aug. 1, 1933; *Chem. Abs.*, 1933, **27**, 4888.

[50] U. S. Patent 1,128,804, Feb. 16, 1915; assigned to Badische Anilin- und Soda-Fabrik; *Chem. Abs.*, 1915, **9**, 1098. Badische Anilin- und Soda-Fabrik, French Patent 463,114, 1913; *J.S.C.I.*, 1914, **33**, 313; British Patent 12,978, 1913; *J.S.C.I.*, 1914, **33**, 593; German Patent 296,866, 1914. See also Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930, 774.

[51] Badische Anilin- und Soda-Fabrik, German Patent 306,301, 1914; addition to 296,866; *J.S.C.I.*, 1920, **39**, 335A. See also I. G. Farbenindustrie A.-G., British Patent 301,969, 1927; *Brit. Chem. Abs.* **B**, 1929, 120; British Patent 288,662, 1926; *Brit. Chem. Abs.* **B**, 1928, 437; German Patent 554,551, 1928; *Chem. Abs.*, 1932, **26**, 5962; British Patent 254,713, 1926; *Brit. Chem. Abs.* **B**, 1927, 644.

The use of a nickel catalyst with promoters (the oxides of titanium, cerium, zinc, molybdenum, chromium, beryllium, uranium, zirconium, manganese, cadmium, calcium and other metals) at temperatures below 700° C. has been proposed by Williams.[53] The catalysts are prepared from the nitrates of the metals which should be free of chlorides and sulphides as these two classes of compounds poison the catalyst. The addition of salts of the rare earth metals, particularly those belonging to the cerium group, is recommended by Chaffette.[54] One method of preparing a catalyst from nickel nitrate has been described by Al[55] and consists in treating the nitrate with somewhat less than the theoretical quantity of sodium hydroxide, followed by reduction of the nickel compound so formed with hydrogen.

Magnesium oxide, impregnated with the oxides of nickel, cerium, or aluminum, has also been suggested.[56] Since the carbon dioxide formed during the reaction between the hydrocarbons and steam is absorbed by the magnesium oxide it is necessary occasionally to regenerate the catalyst by calcining to expel the carbon dioxide. The use of calcium or cerous oxide has also been recommended by others.[57] Cerous oxide absorbs carbon dioxide at 100° C. and can be regenerated by heating the resulting carbonate to 350° to 500° C.

Bergius[58] described a method for the production of hydrogen (for hydrogenation purposes) from gases containing methane (especially from the waste gas from hydrogenation processes) by treatment with steam at 1100° C. In a second stage carbon monoxide is converted to dioxide by reaction with more steam at a lower temperature.

The decomposition of hydrocarbon mixtures with air and steam in the presence of an iron-chromium alloy at high temperatures (1200° to 1300° C.) has been proposed by Clancy.[59]

Casale[60] described a process for the conversion of methane into carbon monoxide and hydrogen by passing a mixture of methane, steam and oxygen through a reaction chamber maintained at 1100° to 1300° C. According to Casale, industrial success with this reaction will be obtained only when conditions in the reaction chamber are such that the final concentration of methane is practically nil. These conditions are said to be realized when the system of the reacting gases: (1) is maintained at pressures below atmospheric; (2) attains a temperature of above 1000° C.; and (3) contains a large excess of steam above that required for reaction.

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[52] In one process (Badische Anilin- und Soda-Fabrik, German Patent 403,049, 1922; *Brit. Chem. Abs.* B, 1925, 71; British Patent 231,218, 1923; *Brit. Chem. Abs.* B, 1925, 357; British Patent 266,410, 1925; *Brit. Chem. Abs.* B, 1927, 316) hydrocarbon gases are treated with water vapor, with or without the addition of carbon dioxide, to produce hydrogen and carbon monoxide. The mixture of gases thus obtained is subsequently used for the synthesis of methyl alcohol.

[53] U. S. Patent 1,826,974, Oct. 13, 1931; *Chem. Abs.*, 1932, 26, 568; U. S. Patent 1,830,010, Nov. 3, 1931; *Chem. Abs.*, 1932, 26, 813; U. S. Patents 1,834,115 and 1,834,116, Dec. 1, 1931; *Chem. Abs.*, 1932, 26, 1402; patents assigned to DuPont Ammonia Corp.

[54] French Patent 734,032, 1932; *Chem. Abs.*, 1933, 27, 1111; Belgian Patent 287,296, 1932; *Chem. Abs.*, 1933, 27, 1463.

[55] U. S. Patent 1,863,681, June 21, 1932; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, 26, 4424.

[56] Beekley, U. S. Patent 1,799,452, Apr. 7, 1931; assigned to DuPont Ammonia Corp.; *Brit. Chem. Abs.* B, 1931, 1094.

[57] I. G. Farbenindustrie A.-G., British Patent 291,244, 1927; *Brit. Chem. Abs.* B, 1928, 523; Swiss Patent 127,030, 1927; *Chem. Abs.*, 1929, 23, 1225.

[58] U. S. Patent, 1,699,177, Jan. 15, 1929. Canadian Patent 263,477, 1926; *Chem. Abs.*, 1926, 20, 3799. British Patent 244,730, 1925; *Brit. Chem. Abs.* B, 1927, 66. See also, Internationale Bergin-Comp. voor Olie- en Kolen-Chemie, British Patent 216,882, 1924; *J.S.C.I.*, 1925, 492B.

[59] Canadian Patent 215,385, 1922; *Chem. Abs.*, 1922, 16, 1136. See also Nitrogen Corp., British Patent 163,703, 1921; *Chem. Abs.*, 1922, 16, 799.

[60] U. S. Patent 1,734,559, Nov. 5, 1929. British Patent 274,610, 1926; *Chem. Abs.*, 1928, 22, 2246. *Cf.* Canadian Patent 285,619, 1928, and Austrian Patent 111,555, 1928.

A process has been proposed by Schmidt and Niemann[61] in which hydrocarbons, alone or mixed with other gases not containing free oxygen, are treated with steam at 300° to 600° C. in the presence of nickel, cobalt or iron activated with difficultly reducible oxides of chromium, vanadium, potassium, magnesium, aluminum, or alkaline earth metals. The reaction may be performed in stages by transforming some of the hydrocarbons, removing the carbon dioxide, and repeating the succession of operations with the hydrogen-hydrocarbon mixture until all the hydrocarbons have been converted. Porter[62] similarly treated a hydrocarbon gas with steam, and after removing the reaction products, subjected them to further treatment with another body of catalyst.

In another method of decomposing hydrocarbons with water vapor,[63] the hot gases after reaction are cooled by water. The water which thus becomes heated is brought into contact with fresh hydrocarbon gases which, thus saturated with water vapor, are introduced into the decomposition chamber.

The production of hydrogen from hydrocarbons, particularly methane, and steam (preferably in excess) by allowing the heated gases to react in successive stages in the presence of catalysts has also been suggested by the Union Chimique Belge, Soc. Anon.[64]

Blake[65] developed a process in which methane and steam in proper proportions are allowed to react in the presence of a catalyst, such as nickel-ceria-alumina, at temperatures ranging from 400° C. to 700° C. to produce hydrogen and carbon dioxide with little or no carbon monoxide. Thus, using 10 volumes of steam to 5 volumes of CH_4 at 508° C., a 90 per cent conversion of the methane was observed and the dry gaseous products contained only 2 per cent of carbon monoxide (after removal of CO_2).

Unsaturated hydrocarbons in a gas mixture which is to be used for the production of hydrogen are reduced by Williams[66] in a prior catalytic treatment with hydrogen or by adding hydrogen to the mixture and allowing the reduction to proceed simultaneously with the decomposition. For the reaction with steam, nickel chromate is used.

Burwell[67] suggested heating hydrocarbons and steam at 1050° to 1150° C. to produce a mixture of hydrogen, carbon monoxide, carbon and hydrocarbons. Carbon is removed by settling and liquid hydrocarbons by scrubbing with water. Hydrocarbons, similar to methane, are converted into carbon monoxide and hydrogen by heating the moist mixture at 1230° to 1280° C., carbon monoxide being converted into dioxide by adding an excess of oxygen to the dried gases and passing them over manganese dioxide catalyst below 100° C. Any oxygen remaining is removed by passing the gases over heated copper, and carbon dioxide is absorbed in solutions of caustic alkalies.

Mixtures of air, oxygen, or carbon dioxide, and steam, with gaseous, liquid or solid carbonaceous materials may be made to react in an electric arc.[68] The gas mixtures thus obtained are further treated with steam, the carbon monoxide reacting to yield hydrogen and carbon dioxide. The carbon dioxide and other impurities are then removed from the product. A mixture of nitrogen and hydrogen which may be used for the synthesis of ammonia is obtained by using air as the oxidizing agent and subsequently adding hydrogen (prepared, for example, by a similar process using carbon dioxide instead of air) to adjust the mixture to the correct proportions. By passing gas mixtures containing hydrocarbons through an electric arc, or by incompletely oxidizing them, they are converted to unsaturated hydrocarbons. After removal of the unsaturated hydrocarbons, the resulting gases can be heated with steam to obtain a mixture of hydrogen and carbon monoxide.[69]

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[61] U. S. Patent 1,882,977, Oct. 18, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 816. German Patent 546,205, 1926; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 3341; I. G. Farbenindustrie A.-G., British Patent 267,535, 1927; *Brit. Chem. Abs.* **B**, 1928, 858.

[62] U. S. Patent 1,874,801, Aug. 30, 1932; assigned to Atmospheric Nitrogen Corp.; *Chem. Abs.*, 1932, 26, 6079.

[63] I. G. Farbenindustrie A.-G., British Patent 265,989, 1927; *Brit. Chem. Abs.* **B**, 1927, 900.

[64] British Patent 357,956, 1931; *Brit. Chem. Abs.* **B**, 1931, 1130; *Chem. Abs.*, 1932, 26, 4922.

[65] U. S. Patent 1,713,325, May 14, 1929; assigned to Lazote, Inc. *Cf.* Beekley, U. S. Patent 1,711,036, April 30, 1929; assigned to Lazote, Inc.

[66] U. S. Patent, 1,673,032, June 12, 1928; assigned to Lazote, Inc.

[67] U. S. Patent 1,689,858, Oct. 30, 1928; assigned to Alox Chemical Corp.; *Brit. Chem. Abs.* **B**, 1929, 172.

It has also been proposed[70] to pass a mixture of 1.8 parts of methane, 2.8 parts of air, and 0.6 part of carbon dioxide through an electric arc of 2.6 amperes at 1,400 volts. The products are treated with steam in the presence of nickel and the carbon dioxide, produced by the conversion of the carbon monoxide, is removed by absorption. The resulting hydrogen-nitrogen mixture is in the correct proportion for the synthesis of ammonia.

Another procedure[71] is that of treating methane with steam in proportions and under conditions such that the resulting gases contain 2 to 15 per cent (best about 4 to 5 per cent) of unchanged methane. The methane is subsequently removed (for example, by combustion with oxygen or along with carbon dioxide by extraction with gasoline under pressure). Elimination of the carbon monoxide from the products may be facilitated by converting the greater part of it, prior to the removal of the undesired gases, into carbon dioxide and hydrogen by reaction with steam. The remainder may be converted to methane by catalytic reduction and removed.

A process for the manufacture of carbon monoxide and hydrogen by oxidizing hydrocarbons (for example, methane) with steam and air in a reaction chamber in the absence of catalysts has been reported by the Union Chimique Belge, Soc. Anon.[72] Pallemaerts[73] suggested preheating the air and gas in separate chambers. The I. G. Farbenindustrie A.-G.[74] proposed to conduct the reaction of methane with air and steam in a water-gas producer in which coal or coke is being gasified at 800° to 1000° C.

Several methods have been described for the production of hydrogen from hydrocarbon gases, particularly refinery gases containing 2 to 10 per cent of unsaturated gases and freed from the major portion of the sulphur compounds originally present. The hydrocarbon gas is passed with an excess of steam through an elongated catalytic zone at high temperatures (650° to about 1100° C.), the direction of flow of the gas mixture being periodically reversed. The reactants are then passed to a second reaction zone where the carbon monoxide is converted by reaction with more steam into carbon dioxide and hydrogen.[75] The catalyst (nickel, or an oxide of nickel and alumina) used in the first stage of the process at temperatures above 650° C. may be reactivated by passing steam, free from hydrocarbon gas, over it at 650° C. for from 6 to 24 hours.[76] Alternatively,[77] reactivation of the catalyst is effected by passing a mixture of oxygen, nitrogen and carbon dioxide, or air and steam, over the heated catalyst for several hours.

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[68] I. G. Farbenindustrie A.-G., British Patent 307,529, 1927; *Brit. Chem. Abs.* **B**, 1929, 393. Yokota (Japanese Patent 95,140, 1932; assigned to the Minister of the Navy; *Chem. Abs.*, 1933, 27, 2770) proposed manufacturing hydrogen by passing steam and hydrocarbons over electrically heated metals and alloys.

[69] I. G. Farbenindustrie A.-G., British Patent 269,547, 1927; *Brit. Chem. Abs.* **B**, 1928, 291.

[70] I. G. Farbenindustrie A.-G., British Patent 322,701, 1929; addition to British Patent 307,529, 1927; *Brit. Chem. Abs.* **B**, 1930, 143.

[71] I. G. Farbenindustrie A.-G., British Patent 319,957, 1928; *Brit. Chem. Abs.* **B**, 1929, 1014. *Cf.* Wietzel and Schiller, U. S. Patent 1,921,856, Aug. 8, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 5158; Wietzel, Haller and Hennicke, German Patent 558,430, 1926; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 381.

[72] British Patent 343,172, 1929; *Brit. Chem. Abs.* **B**, 1931, 433. *Cf.* British Patent 341,393; *Brit. Chem. Abs.* **B**, 1931, 331.

[73] British Patent 360,148, 1930; assigned to Union Chimique Belge; *Chem. Abs.*, 1933, 27, 574.

[74] British Patent 336,635, 1929; *Brit. Chem. Abs.* **B**, 1931, 103. British Patent 336,944, 1929; *Brit. Chem. Abs.* **B**, 1931, 288. *Cf.* Odell, British Patent 386,981, 1931; *Brit. Chem. Abs.* **B**, 1933, 339; U. S. Patent 1,762,100, June 3, 1930; assigned to Columbia Engineering and Management Corp.; *Brit. Chem. Abs.* **B**, 1931, 287.

A catalyst for the reaction of gaseous hydrocarbons, of higher molecular weight than methane, with steam at 400° to 1000° C. can be prepared, according to Hüttner and Wietzel,[78] by making a paste of a mixture containing at least one metal (or its oxide, hydroxide or carbonate) of the iron group together with a difficultly reducible oxide of a metal of Groups II to VI of the periodic system and a hydraulic binding agent. The paste is allowed to set before use. In the treatment of such gaseous hydrocarbons with steam at 400° to 1000° C., it is said to be advantageous [79] to use more than one layer of the catalyst, each succeeding layer having a higher activity, and being maintained at a lower temperature than the preceding one. Thus, if the first layer consists of a metal of the iron group made into an aqueous paste with a hydraulic binding agent, the next layer may consist of a similar group metal, activated, however, by the addition of a non-reducible oxide of a metal of Groups II to VI.

Williams [80] conducted a mixture of steam and gaseous hydrocarbons, such as methane, through a series of reaction vessels containing a number of superimposed trays on which the catalyst is placed. The temperature for the reaction is maintained by admitting small quantities of air to the free spaces just above each tray so that only a small part of the mixture is converted into hydrogen and carbon monoxide at every stage of the treatment. Overheating and undesirable side reactions are thus avoided.

Another proposed catalyst consists of nickel, cobalt, or iron mixed with aluminum compounds containing oxygen and at least one of the following elements: silicon, hydrogen, carbon, boron, phosphorus and sulphur (for example, kaolin), together with magnesium or an alkaline earth oxide.[81] The addition of phosphorus pentoxide to the nickel oxide-aluminum oxide catalysts has been recommended.[82]

Schulz and Eisenstecken [83] used catalysts of iron, cobalt, nickel, chromium, aluminum, manganese, copper, vanadium, tungsten, or their alloys with each other and effected the reaction of hydrocarbon gases with steam at 1000° C. in a channel of carborundum. The heat necessary for reaction is generated by induced high-frequency electric current. The catalyst or conveniently shaped metallic masses are placed in the reaction space to receive the electrical energy.

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[75] Standard-I. G. Co., British Patent 366,360, 1932. Hanks and Freyermuth, U. S. Patent 1,915,363, June 27, 1933; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 4360. For the purification of the gases previous to catalytic treatment see, Freyermuth, U. S. Patent 1,904,439, Apr. 18, 1933; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 3568.

[76] Standard-I. G. Co., French Patent 711,813, 1931; *Chem. Abs.*, 1932, **26**, 2022. British Patent 364,419, 1931; *J. Inst. Pet. Tech.*, 1932, **18**, 102A. *Cf.* Freyermuth, Small and Hanks, U. S. Patent 1,904,441, Apr. 18, 1933; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 3589.

[77] Standard-I. G. Co., French Patent 715,792, 1931; *Chem. Abs.* 1932, **26**, 2023. British Patent 366,369, 1931; *J. Inst. Pet. Tech.*, 1932, **18**, 135A. *Cf.* Hanks and Small, U. S. Patent 1,915,362, June 27, 1933; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 4360.

[78] German Patent 552,446, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 4422. I. G. Farbenindustrie A.-G., British Patent 376,358, 1931; *Brit. Chem. Abs.* **B**, 1932, 936. French Patent 729,119, 1931; *Chem. Abs.*, 1932, **26**, 6079. See also I. G. Farbenindustrie A.-G., British Patent 360,081, 1930; *Brit. Chem. Abs.* **B**, 1932, 62. *Cf.* Bataafsche Petroleum Maatschappij, British Patent 381,072, 1932; *Chem. Abs.*, 1933, **27**, 4039; French Patent 731,652, 1932; *Chem. Abs.*, 1933, **27**, 816.

[79] I. G. Farbenindustrie A.-G., British Patent 379,014, 1931; *Brit. Chem. Abs.* **B**, 1932, 981.

[80] U. S. Patent 1,736,065, Nov. 19, 1929; assigned to DuPont Ammonia Corp.; *Chem. Abs.*, 1930, **24**, 697; *Brit. Chem. Abs.* **B**, 1930, 143.

[81] I. G. Farbenindustrie A.-G., British Patent 323,855, 1928; *Brit. Chem. Abs.* **B**, 1930, 231.

[82] Standard Oil Development Co., German Patent 534,906, 1930; *Chem. Abs.*, 1933, **27**, 1110.

[83] British Patent 314,870, 1929; assigned to Verein. Stahlwerke A.-G.; *Brit. Chem. Abs.* **B**, 1931, 288.

Other catalysts which have been suggested for the reaction of hydrocarbons and steam are the oxides of zirconium, aluminum, thorium and titanium.[84] The temperature is maintained above 900° C. when these are used.

APPLICATION OF THE STEAM REACTION IN THE "REFORMING" OF GASEOUS HYDROCARBONS

An important new application of the hydrocarbon-steam reaction is in the reforming of hydrocarbon gases, such as propane and butane, to yield gas mixtures having heating values and specific gravities similar to those of natural and coal-carbonization gases. By treating butane, for example, with steam in the presence of a catalyst, combustible gases can be obtained with calorific values ranging from 260 to 1800 B.t.u. depending upon the steam:hydrocarbon ratio, the temperature, and time of contact with the catalyst. On account of its great flexibility, such a reforming process is of value in supplying a gas useful to supplement natural gas supplies during periods of peak load. Oberfell and Guyer[85] gave the analyses in Table 71 of various gases made from butane by this steam-reforming process which show its utility for duplicating the qualities of other commercial gaseous fuels. The process is said to be applicable to low-boiling petroleum hydrocarbons.

TABLE 71.—*Analyses of Gases from the Reforming of Butane by the Steam Reaction.*

	1	2	3	4	5
Specific gravity	0.45	0.52	0.55	0.62	0.86
B.t.u. value (gross)	453	609	666	809	1266
CO_2, % (by volume)	7.2	3.6	6.4	5.0	4.6
CO, %	18.2	13.3	15.0	15.0	10.4
H_2, %	55.4	47.7	44.9	43.6	38.1
Unsaturated hydrocarbons, %	4.3	8.3	9.5	12.9	13.3
Saturated hydrocarbons, %	14.9	27.1	24.2	23.5	33.6

FORMATION OF HYDROCYANIC ACID BY THE REACTIONS OF HYDROCARBONS WITH NITROGEN, AMMONIA, AND OXIDES OF NITROGEN

The production of hydrocyanic acid and cyanides from paraffin hydrocarbons, particularly from methane, has attracted much attention. The processes for making hydrocyanic acid from hydrocarbons vary. Mixtures of hydrocarbons (or carbon monoxide) with nitrogen or air, with ammonia and with the oxides of nitrogen have been suggested.

In this connection it may be well to mention briefly one early general method which has been used for the production of cyanides.[86] Desfosses[87] in 1828 observed the formation of sodium cyanide in small quantities on passing atmospheric nitrogen through a highly heated mixture of carbon and sodium carbonate. During the early part of the nineteenth century processes for producing cyanides from coal and air in the presence of alkalies and catalysts were developed.[88] The reaction represented by the equation:

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[84] Matignon and Séon, French Patent 713,487, 1931; *Chem. Abs.*, 1932, **26**, 1728; *Compt. rend.*, 1933, **196**, 77; *Brit. Chem. Abs.* **A**, 1933, 254; *Compt. rend.*, 1932, **195**, 1345; *Chem. Abs.*, 1933, **27**, 1565.

[85] *Refiner*, 1932, 11, 371; *Chem. Abs.*, 1932, **26**, 4443. *Oil and Gas J.*, June 9, 1932; see also Guyer, Setrum and Huppke, *Gas Age-Record*, 1932, **69**, 683, 700; *Chem. Abs.*, 1932, **26**, 5731; and Faber, *Western Gas*, 1932, **8**, 7, 39; *Chem. Abs.*, 1932, **26**, 5196.

[86] For a detailed history and description of the cyanide industry see Robine and Lenglen, "L'industrie des cyanures," Librairie Polytechnique, Paris, 1903; Thorpe, "Dictionary of Applied Chemistry," Longmans, Green and Co., London, 1912, 2, 193, 196; Gmelin, "Handbook of Chemistry," Translated by Watts, Cavendish Society, London, 1852, 7, 378.

[87] *Ann. chim. phys.*, 1828, **38**, 158; *J. Pharm.* 1828, **14**, 280.

$$Na_2CO_3 + 4C + N_2 \longrightarrow 2NaCN + 3CO - 138{,}500 \text{ cals.}$$

requires a temperature of the order of 1400° C. in the absence of catalysts.[89] Bucher[90] later proposed briquetting the mixture of sodium carbonate and coke with a catalyst consisting of metallic iron. Under these conditions nitrogen is readily absorbed at 920° to 950° C., yielding briquettes containing 26 to 30 per cent of sodium cyanide. According to Thompson,[91] a pure form of carbon such as produced by the thermal decomposition of hydrocarbons (lampblack or petroleum coke) or of carbon monoxide is superior to coke from coal for this purpose.

These processes in which coal or coke is the source of carbon were followed by others in which the carbon was supplied by hydrocarbons or oxides of carbon. This allowed the production of hydrocyanic acid entirely in the gaseous phase. Other gaseous nitrogen compounds such as ammonia and oxides of nitrogen were also substituted for the nitrogen. A large number of such procedures has been described since about 1840. Only those of more recent date in which hydrocarbons are used will be mentioned.

REACTION OF HYDROCARBONS WITH NITROGEN

The direct reaction of hydrocarbons with nitrogen to form hydrocyanic acid according to the equation, $2CH_4 + N_2 \rightarrow 2HCN + 3H_2$, requires very high temperatures for appreciable yields, because of the highly endothermic nature of the change. This reaction was observed by Berthelot[92] as taking place in the electric arc. Bone and Jerdan,[93] by the prolonged action of an electric discharge on methane mixed with traces of nitrogen, obtained a gas containing 0.8 per cent of hydrocyanic acid. The formation of hydrocyanic acid from nitrogen and hydrocarbons in an electric arc has also been discussed by Moscicki,[94] Koenig and Hubbuch[95] and Küster.[96]

The formation of alkaline cyanides and ammonia was observed by Fogarty[97] on conducting nitrogen and alkalies into a retort in which acetylene and other hydrocarbon vapors are being cracked. The hydrocarbon vapors are passed into the retort together with a stream of finely powdered alkali or alkaline earth.. In another process Fogarty[98] used producer gas. Colin[99] described a method of making cyanides and ammonia by passing air and fuel gas under pressure into a furnace. A volatile hydrocarbon is then introduced into the flame. The hydro-

[88] Thompson, *Mechanics Magazine*, 1839, No. 822 (May 11), 92. Also *Dinglers polytech. J.*, 1839, **23**, 281. See Bucher, *Ind. Eng. Chem.*, 1917, **9**, 233. See also Possoz and Boissière, British Patent 9,985, 1843; Mactear, British Patent 5,143, 1879; *Chem. Zentr.*, 1882, **1**, 607.

[89] Mond, British Patent 433, 1882; *J.S.C.I.*, 1882, **1**, 364.

[90] *Ind. Eng. Chem.*, 1917, **9**, 233. Bucher also discusses various other proposed processes of this type.

[91] *Chem. Met. Eng.*, 1922, **26**, 124. In this article some of the studies which have been made of this process are reviewed.

[92] *Compt. rend.*, 1868, **67**, 1132; *Ann. chim. phys.*, 1868, (4) **13**, 143; *Ann.*, 1869, **150**, 60. See also *Chem. Zentr.*, 1870, **1**, 226.

[93] *J.C.S.*, 1897, **71**, 59.

[94] *Z. Elektrochem.*, 1911, **17**, 877; *Chem. Soc. Abs.*, 1911, **100** (2), 1057; Lipinski (*Z. Elektrochem.*, 1911, **17**, 761; *Chem. Soc. Abs.*, 1911, **100** (2), 849) reported data obtained while working in Moscicki's laboratory.

[95] *Z. Elektrochem.*, 1922, **28**, 202; *Chem. Soc. Abs.*, 1922, **122** (1), 642.

[96] *Brennstoff-Chem.*, 1931, **12**, 329; *Brit. Chem. Abs.* **B**, 1931, 1008.

[97] U. S. Patent 500,651, July 4, 1893.

[98] U. S. Patent 615,266, Dec. 6, 1898.

[99] U. S. Patent 598,195, Feb. 1, 1898.

cyanic acid thus produced is absorbed from the ascending current of incandescent gases by introducing a stream of finely powdered alkali or alkaline earth.

Gow[100] proposed mixing natural gas (containing 95 per cent of methane) with nitrogen or air and conducting the mixture through an electric arc. Best results were obtained with a spluttering arc.

By introducing a mixture of superheated nitrogen and a liquid hydrocarbon or acetylene into a fused mixture of sodium and potassium hydroxide at 300° C., Blackmore[101] obtained cyanides.

Sinding-Larsen[102] passed a mixture of nitrogen and the vapors of hydrocarbons over heated aluminum or silicon and obtained the nitrides of these metals together with volatile products containing ammonia and hydrocyanic acid.

Moscicki and Jablczynski[103] proposed to manufacture hydrocyanic acid by repeatedly heating a gas mixture containing nitrogen, hydrogen and a hydrocarbon at high temperatures, followed by cooling. The excess hydrogen is removed from time to time. The heating was effected in an electric furnace having a revolving high-tension flame, the temperature reaching 2500° to 3500° C.

Lipinski[104] synthesized hydrocyanic acid by conducting a mixture of oil gas and nitrogen over an extended flaming arc. After removing the resulting hydrogen cyanide the remaining mixture was recirculated with a fresh charge. A mixture giving satisfactory yields consists of 10 per cent hydrogen, 20 per cent methane, and 70 per cent nitrogen, according to Malisoff and Egloff.[105] A large excess of nitrogen is necessary to prevent the separation of free carbon. To produce long steady arcs and to catalyze the reaction, conducting vapors of metals or metallic compounds, such as copper or iron or their salts, can be introduced into the zone of electrical discharge.[106]

A process for making hydrocyanic acid from nitrogen, hydrogen and hydrocarbons under a pressure of about 1.6 atmospheres in an electric furnace containing a voltage arc was described by Liebknecht.[107] He produced 50 grams of hydrocyanic acid per kilowatt-hour of electricity from a mixture of 5.3 per cent carbon monoxide, 8.3 per cent methane, 33.7 per cent hydrogen, and 42.7 per cent nitrogen.

For the preparation of hydrocyanic acid, Muthmann and Schaidhauf[108] used an apparatus[109] consisting of a 1500 cc. glass retort with four side tubes, two of which carried electrodes and two served as inlet and outlet. An excess pressure of about 40 cm. of mercury was maintained in the apparatus and the power source was an alternating current of 50 cycles at 93 volts and a maximum of 43 amperes. The electrodes consisted of silver, gold and platinum screwed into cooled copper rods. The reaction between methane and nitrogen by this method gave hydrocyanic acid, equivalent in amount to the methane present, and hydrogen.

Hydrocyanic acid can be made, according to Helfenstein,[110] by introducing equal volumes of acetylene and nitrogen through a hollow vertical electrode into a molten slag bath on which there is a layer of animal charcoal.

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[100] U. S. Patent 801,782, Oct. 10, 1905; assigned to G. Westinghouse; *J.S.C.I.*, 1906, **25**, 29.

[101] U. S. Patents 889,096 and 889,097, May 26, 1908; *Chem. Abs.*, 1907, **2**, 2850.

[102] U. S. Patent 1,042,723, Oct. 29, 1912; assigned to Storm, Bull & Co.; *J.S.C.I.*, 1912, **31**, 1126; French Patent 414,837, 1910; *J.S.C.I.*, 1910, **29**, 1205.

[103] U. S. Patent 1,050,978, Jan. 21, 1913; assigned to Aluminium-Industries A.-G.; *J.S.C.I.*, 1913, **32**, 195; *Chem. Abs.*, 1913, **7**, 735. French Patent 417,794, 1910; *J.S.C.I.*, 1911, **30**, 26.

[104] British Patent 11,107, 1914; *Chem. Abs.*, 1915, **9**, 3176; *J.S.C.I.*, 1915, **34**, 612. German Patent 285,931, 1909; *Chem. Abs.*, 1916, **10**, 1473. Austrian Patent 71,147, 1916; *Chem. Abs.*, 1916, **10**, 2505. *Cf.* Soc. d'Electro-Chimie, French Patent 458,546, 1912; *J.S.C.I.*, 1913, **32**, 1108.

[105] *J. Phys. Chem.*, 1918, **22**, 529.

[106] Consortium für Elektrochemische Industrie G.m.b.H., German Patent 268,277, 1911; *J.S.C.I.*, 1914, **33**, 200; addition to German Patent 263,692, 1911; *J.S.C.I.*, 1913, **32**, 1067.

[107] U. S. Patents 1,235,342 and 1,235,343, July 31, 1917; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1917, **11**, 2564; British Patent 181,058, 1921; assigned to Deutsche Gold- und Silber-Scheideanstalt (vorm. Roessler); *J.S.C.I.*, 1922, **41**, 589A.

[108] *Z. Elektrochem.*, 1911, **17**, 497; *Chem. Abs.*, 1911, **5**, 3010.

[109] Apparatus substantially the same as that used by Muthmann and Hofer, *Ber.*, 1903, **36**, 438.

[110] U. S. Patent 1,169,817, Feb. 1, 1916; *Chem. Abs.*, 1916, **10**, 859; German Patent 262,325, 1911; *Chem. Abs.*, 1913, **7**, 3720.

Starke and Starke[111] described an apparatus in which cyanides are produced by passing a mixture of methane and nitrogen or air above 600° C. over a catalyst. The catalyst is formed by calcining a mixture of magnesium oxide, potassium carbonate, metallic iron, and acetic acid.

By injecting ammonia into heated natural gas or other hydrocarbon, Poindexter[112] obtained hydrocyanic acid. The natural gas, kerosene vapor or other hydrocarbon material may be mixed first with ammonia and then introduced into an externally heated zone.[113] The heated zone can be a glazed fireclay tube through which the gases are passed at such a rate that they are exposed for about one second to a temperature of 1200° C.[114]

According to the I. G. Farbenindustrie A.-G., the production of acetylene from hydrocarbons and hydrocyanic acid from mixtures of nitrogen and hydrocarbons in the electric arc can be combined. Thus,[115] in the treatment of gas mixtures containing hydrocarbons and nitrogen, a furnace is used having a central electrode and an annular or tubular electrode through which the gases are passed. An insulating mantle is arranged between the electrodes to allow for adjustment of the length of the arc to that most favorable to the reaction. Acetylene and hydrocyanic acid may be obtained by the action of the discharge on residual gases from synthetic ammonia or other hydrogenation plants, carbon monoxide being preferably removed first by catalytic reduction to methane.[116] The gases entering the arc are preheated by gases leaving it.

The simultaneous production of acetylene and hydrocyanic acid from methane and nitrogen by subjecting the gaseous mixture to an electric discharge has been mentioned by Küster.[117] With a load of 1.6 kilowatts and a gas mixture containing 15 to 25 per cent methane under a pressure of 10 to 15 mm., the resulting gas was found to contain about 10 per cent hydrocyanic acid.

Bagley[118] produced hydrocyanic acid by bringing nitrogen into contact with a bath of hydrocarbon oil under the surface of which an electric arc is maintained.

Ammonia together with hydrocyanic acid is produced when a mixture of gaseous hydrocarbons, nitrogen, and hydrogen is passed under pressures of from 1 to 350 atmospheres over alkaline earth cyanamides at temperatures varying from 200° C. to 1000° C. An example of such a process[119] is the passage of coke-oven gas, containing principally methane, nitrogen and hydrogen, over calcium cyanamide at 750° C.

REACTIONS OF HYDROCARBONS WITH AMMONIA

It has long been known[120] that by passing ammonia over heated carbon, hydrocyanic acid is formed according to the equation

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[111] U. S. Patent 1,206,155, Nov. 28, 1916; *Chem. Abs.*, 1917, 11, 193.

[112] U. S. Patent 1,387,170, Aug. 9, 1921; *Chem. Abs.*, 1921, 15, 3897.

[113] Poindexter, U. S. Patent 1,562,914, Nov. 24, 1925; *Chem. Abs.*, 1926, **20**, 481.

[114] Poindexter, U. S. Patent 1,584,137, May 11, 1926; *Chem. Abs.*, 1926, **20**, 2050.

[115] British Patent 294,494, 1927; *Brit. Chem. Abs.* **B**, 1928, 738.

[116] British Patent 306,008, 1927; *Brit. Chem. Abs.* **B**, 1929, 313.

[117] *Brennstoff-Chem.*, 1931, **12**, 329; *Brit. Chem. Abs.* **B**, 1931, 1008. See also Peters and Wagner, *Brennstoff-Chem.*, 1931, **12**, 67; *Brit. Chem. Abs.* **B**, 1931, 429.

[118] U. S. Patent 1,731,331, Oct. 15, 1929; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1930, **24**, 209.

[119] Societe d'Etudes Chimiques pour L'Industrie, Swiss Patent 143,982, 1929; *Chem. Abs.*, 1931, **25**, 4092.

[120] Clouet, *Annales de Chimie*, 1791, 11, 30. Also Crell's *Chemische Annalen*, 1796, 1, 45. Bonjour, *J. de l'Ecole Polytechnique*, 1797, 3. 436. Also Scher's *Allgemeines J. der Chemie*, 1799, 2, 621. Langlois, *Annales de Chimie et Physique*, 1812, 76, 111; Gay-Lussac's *Annales de Chimie et Physique*, 1816, 1, 117. Liebig's *Annalen der Pharmacie*, 1842, **36**, 65. Erdmann's *J. praktische*

$$NH_3 + C \longrightarrow HCN + H_2$$

In the presence of an excess of ammonia the hydrocyanic acid appears, of course, in the form of its ammonium salt. The reaction is an endothermic one and requires high temperatures for appreciable yields. Badger[121] investigated the equilibrium at a temperature of 800° Absolute (527° C.). The values of the equilibrium constant

$$K = \frac{p_{H_2} \times p_{HCN}}{p_{NH_3}}$$

at 800° Absolute averaged 5.8×10^{-6}. From existing data the heat content of hydrocyanic acid was calculated to be 30,500 calories at 18° C. and 30,400 calories at 800° Absolute and the free energy as 28,400 calories at 800° Absolute.

Hutton and Smith[122] showed that hydrocyanic acid is also formed when a mixture of hydrogen and nitrogen is heated at 1700° C. in the presence of carbon. Von Wartenburg[123] studied the equilibrium existing in this reaction.[124]

In a similar way ammonia and various hydrocarbons can react to form hydrocyanic acid and hydrogen. The reaction of methane may be represented by the equation:

$$CH_4 + NH_3 \longrightarrow HCN + 3H_2$$

Here again we are dealing with an endothermic reaction, so that high temperatures are necessary to obtain appreciable yields. In purely thermal processes, moreover, it is probably necessary to employ high temperatures in conjunction with short heating periods (exactly as in the case of the production of acetylene from methane by pyrolysis).

The formation of hydrocyanic acid by the reaction of ammonia with methane, ethylene, and acetylene at temperatures above 700° C. in the presence of contact materials has been systematically investigated by Bredig, Kortüm, Elöd, Müller, and Demme.[125] With rising reaction temperatures, the yields of hydrocyanic acid were found to increase to a maximum and thereafter decline. The reaction between ethylene and ammonia is actively catalyzed by a mixture of quartz and clay or by pure clay granules, and the highest yields of hydrocyanic acid are obtained by using equimolecular quantities of reactants. In the reaction between acetylene and ammonia, the yield of hydrocyanic acid at any one temperature was found to be independent of the contact time within the limits studied. Since methane was found to yield hydrocyanic acid only at temperatures which favored the formation of acetylene from this hydrocarbon, it was thought probable that the production of hydrocyanic acid from methane (and from ethylene) and ammonia proceeds through the intermediate formation of acetylene.

Peters and Küster[126] described the formation of hydrocyanic acid from mix-

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Chemie, 1842, **23**, 232. Kuhlmann, *Annalen der Pharmacie*, 1843, **38**, 62. See Gmelin's "Handbook of Chemistry," Cavendish Society, London, 1862, 7, 382. Also de Lambilly, British Patent 1032, 1892; *J.S.C.I.*, 1892, **11**, 604. Bergmann, *J. Gasbel.*, 1896, **39**, 117, 140. *Chem. Zentr.*, 1896, **67** (1), 744, 802. Lance, *Compt. rend.*, 1897, **124**, 819; *Chem. Soc. Abs.*, 1897, **72** (1), 390. Pring and Hutton, *J.C.S.*, 1906, **89**, 1591. Woltereck, French Patent 354,081, 1905; *Chem Abs.*, 1907, **1**, 384. Also see *Compt. rend.*, 1908, **146**, 929; *Chem. Abs.*, 1908, **2**, 1935. von Wartenburg, *Z. anorg. Chem.*, 1907, **52**, 299; *Chem. Soc. Abs.*, 1907, **92** (1), 299. Voerkelius, *Chem. Ztg.*, 1909, **33**, 1025, 1078, 1090; *Chem. Soc. Abs.*, 1909, **96** (1), 776.

[121] *J.A.C.S.*, 1924, **46**, 2166.

[122] British Patent 23,835, 1906; *J.S.C.I.*, 1907, **26**, 1138; *Trans. Amer. Elektrochem. Soc.*, 1908, **13**, 359. Pring and Hutton, *J.C.S.*, 1906, **89**, 1591.

[123] von Wartenburg, *Z. anorg. Chem.*, 1907, **52**, 299; *Chem. Soc. Abs.*, 1907, **92** (1), 299.

[124] See also Wallis, *Ann.*, 1906, **345**, 353; *Chem. Soc. Abs.*, 1906, **90** (1), 730.

[125] *Z. Elektrochem.*, 1930, **36**, 991-1023; *Chem. Abs.*, 1931, **25**, 1176; *Brit. Chem. Abs.* **A**, 1931, 176.

[126] *Brennstoff-Chem.*, 1931, **12**, 122; *Chem. Abs.*, 1931, **25**, 2922.

tures of ammonia and methane by passing them at high gas velocities under diminished pressure through a high-voltage electric discharge. With gas mixtures containing 15 per cent, or less, of either ammonia or methane, a quantitative conversion of the smaller constituent into hydrocyanic acid could be effected. With more powerful discharges the excess methane was partly converted into acetylene and the excess ammonia was decomposed into its elements.

The processes proposed for the production of hydrocyanic acid from gaseous hydrocarbons and ammonia usually involve either heating to high temperatures with catalysts or exposure of the gaseous reactants to an electric discharge.

For example, Lance and de Bourgade[127] proposed to use a mixture of 80 liters of ammonia gas, 2000 liters of gaseous hydrocarbons (acetylene, ethylene or methane) with 200 liters of nitrogen at a red heat in order to obtain hydrocyanic acid. The use of nitrogen or a mixture of nitrogen and hydrogen as diluent gases is said to minimize carbon deposition during the reaction between ammonia and methane at temperatures of 1150° C. or higher at high space velocities.[128]

Beindl[129] suggested the reaction of a volatile nitrogen compound with liquid or gaseous hydrocarbons in the presence of contact materials such as copper or the oxides of iron. According to Beindl, passing a mixture of ammonia and acetylene over a copper catalyst at 480° C. results in the formation of hydrocyanic acid. Similar processes involving the production of hydrocyanic acid or cyanides from ammonia and hydrocarbons have been advanced by Woltereck[130] and de Lambilly.[131]

A gaseous mixture containing ammonia, oxygen and hydrocarbons (aliphatic or aromatic) is passed at a temperature of 700° to 1200° C. over an oxidation catalyst (iridium, platinum, rhodium, palladium, osmium, gold or silver, and the oxides or phosphates of the rare earths) to yield hydrocyanic acid on cooling. The gaseous product may be passed over alkali or alkaline earth metal oxides or hydroxides to form cyanides or cyanamides.[132]

Wheeler[133] reported a method for making hydrocyanic acid in which hydrocarbons (methane or coal gas) are heated to at least 800° C. before or after admixture with nitrogen or ammonia and the hot gaseous mixture is subjected to an arc or spark discharge. Better yields are obtained with an excess of nitrogen or ammonia. The gases used in this process should be free from oxygen.

REACTION OF CARBON MONOXIDE WITH AMMONIA

Kuhlmann[134] observed the formation of hydrocyanic acid when carbon monoxide was passed with ammonia over heated spongy platinum. Considerable interest has been displayed in the production of hydrocyanic acid by this apparently simple reaction of carbon monoxide and ammonia.[135] Thus Liebknecht passed a mixture of carbon monoxide and ammonia over a catalyst composed of a porous non-acid charcoal maintained at 400° to 800° C.[136] Frank and Caro[137] used a mixture of carbon monoxide and ammonia at ordinary or increased pressures. These gases are led over cyanides of the alkaline earths at 700° to 800° C., or over other compounds (such as the oxides, carbonates and others) which can be converted into cyanamides by the action of hydrocyanic acid or of the ammonia-carbon monoxide mixture. The process is carried out in the absence of activated charcoal and of metals catalyzing decomposition. Decomposition may, however, be prevented by the addition of poisoning substances such, for example, as sulphides.

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[127] British Patent 26,326, 1897; *J.S.C.I.*, 1898, **17**, 762. German Patent 100,775, 1897; *Chem. Zentr.*, 1899, **70** (1), 766.

[128] Wheeler, Mills, Fletcher and McAulay, British Patents 335,947, 1929, and 353,407, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 1150; 1931, 924.

[129] German Patent 216,264, 1908; *J.S.C.I.*, 1909, **28**, 1314. German Patent 254,068, 1912; *J.S.C.I.*, 1913, **32**, 24. *Cf.* U. S. Patent 1,144,457, June 29, 1915; *J.S.C.I.*, 1915, **34**, 834.

[130] German Patent 169,032, 1904; *Chem. Zentr.*, 1906, **77** (1), 1304.

[131] British Patent 15,513, 1892; *J.S.C.I.*, 1892, **11**, 1006.

[132] I. G. Farbenindustrie A.-G., British Patent 361,004, 1930; *Brit. Chem. Abs.* **B**, 1932, 101. Also French Patent 715,052, 1931; *Chem. Abs.*, 1932, **26**, 1719.

[133] British Patent 325,860, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 508.

[134] *Annalen der Pharmacie*, 1841, **38**, 62; see Gmelin's "Handbook of Chemistry," Translated by Watts, Cavendish Society, London, 1852, **7**, 382; and Thorpe, "Dictionary of Applied Chemistry," Longmans, Green and Co., London, 1912, **2**, 191. for other historical material.

[135] See also, e.g., Bredig, Elöd and Müller, *Z. Elektrochem.*, 1930, **36**, 991-1023; *Brit. Chem. Abs.* **A**, 1931, 176. Bredig, Elöd and König, *Z. Elektrochem.*, 1931, **37**, 2; *Brit. Chem. Abs.* **A**,

Mittasch and Michael[138] used aluminum oxide as a catalyst. Another procedure is conducting a mixture of carbon monoxide containing 10 to 12 per cent of ammonia over catalysts composed of iron, cobalt, or nickel carbide.[139] The catalyst may also contain molybdenum, tungsten, cerium, titanium, or copper, in the free or combined state.[140] The carbides are made by melting the metals with finely divided carbon. The reaction to form HCN is carried out at a temperature below 600° C. (for example, 450° C.) so that the ammonia is appreciably converted. Internal or external heating may be employed. The hydrocyanic acid is removed either by condensation as ammonium cyanide or by absorption in caustic alkali solution, the residual gases being returned to the process.

To obtain cyanides Wittek[141] treated alkali hydroxides or carbonates in the presence of carbon with ammonia and carbon dioxide mixed with hydrocarbons at temperatures of 400° to 800° C. and at atmospheric or increased pressures. The process is said to be improved by a number of factors: for example, the presence of halides or cyanates; the use of catalysts such as copper, manganese or activated carbon; and the regulation of the water content of the furnace gases.

REACTION OF HYDROCARBONS WITH OXIDES OF NITROGEN

Kuhlmann[142] observed the formation of hydrogen cyanide on treating methane with nitric oxide in the presence of heated spongy platinum. This reaction has apparently not been as thoroughly investigated as that of carbon, carbon monoxide, or hydrocarbons with nitrogen or ammonia. Huntington,[143] however, used this reaction in a process for the production of hydrocyanic acid in which acetylene was mixed with nitric oxide and ignited in a cylinder with an electric spark. The hydrocyanic acid was absorbed in alkali.

1931, 557. de Lambilly, British Patent 16,049, 1890; *J.S.C.I.*, 1891, **10**, 642; British Patent 3,735, 1893; *J.S.C.I.*, 1894, **13**, 38. Mactear, British Patent 5,037, 1899; *J.S.C.I.*, 1900, **19**, 246; French Patent 292,239, 1899; *Chem. Ztg.*, 1900, **24** (2), 1119. U. S. Patents 654,466 and 654,467, July 24, 1900; *Chem. Ztg.*, 1900, **24** (2), 693. Jackson and Laurie, *J.C.S.*, 1905, **87**, 433. Carpenter and Linder, *J.S.C.I.*, 1905, **24**, 63. Bredig and Elöd, British Patents 229,774 and 229,973, 1923; *Chem. Abs.*, 1925, **19**, 3149; *J.S.C.I.*, 1925, 315B; U. S. Patent 1,598,707, Sept. 7, 1926; *Chem. Abs.*, 1926, **20**, 3541.

[136] U. S. Patent 1,626,648, May 3, 1927; assigned to Roessler and Hasslacher Chemical Co.; *Brit. Chem. Abs.* **B**, 1927, 440; British Patent 207,830, 1923; assigned to Deutsche Gold- und Silber-Scheideanstalt (vorm. Roessler); *Chem. Abs.*, 1924, **18**, 1553; British Patent 242,685, 1924; assigned to Deutsche Gold- und Silber-Scheideanstalt (vorm. Roessler); *Chem. Abs.*, 1926, **20**, 3783.

[137] British Patent 282,379, 1927; *Brit. Chem. Abs.* **B**, 1928, 746.

[138] U. S. Patent 1,582,851, April 27, 1926; assigned to B.A.S.F.Co.; *Chem. Abs.*, 1926, **20**, 2050; British Patent 220,771, 1923; *Brit. Chem. Abs.* **B**, 1924, 869. Mittasch discusses catalysis in *Ber.*, 1926, **59**, 13.

[139] I. G. Farbenindustrie A.-G., British Patent 300,369, 1927; *Brit. Chem. Abs.* **B**, 1929, 52.

[140] See also Beindl, U. S. Patents 1,492,193 and 1,492,194, April 29, 1924; *Chem. Abs.*, 1924, **18**, 2059; British Patent 10,321, 1915; *J.S.C.I.*, 1921, **40**, 623A.

[141] British Patent 358,745, 1930; *Brit. Chem. Abs.* **B**, 1931, 1139.

[142] *Annalen der Pharmacie*, 1838, **29**, 284; see Gmelin's "Handbook of Chemistry," Translated by Watts, Cavendish Society, London, 1852, **7**, 381; also Thorpe, *loc. cit.*

[143] British Patent 14,855, 1895; *J.S.C.I.*, 1896, **15**, 594.

Elöd and Nedelmann,[144] examining the action of nitric oxide on methane, ethylene and acetylene, arrived at the following conclusions:

> (1) Hydrocyanic acid is produced by the action of nitric oxide on the above-mentioned hydrocarbons at high temperatures. Under similar conditions the yield of hydrocyanic acid is greater from acetylene than from ethylene, and at the same time the quantity of polymerized substances and of formaldehyde is larger. The reaction temperature required by methane is 300° C. higher than for the other hydrocarbons for similar yields of hydrocyanic acid.
>
> (2) The reaction between nitric oxide and ethylene is catalyzed by various materials, of which the best is a mixture of equal parts of quartz and alumina. Addition of steam to the reaction mixture decreases the yield of hydrocyanic acid and increases the production of ammonia. The addition of hydrogen favors the formation of hydrocyanic acid.
>
> (3) The production of hydrocyanic acid increases greatly with rising temperature and is large at 1000° C. and over. With rising temperatures the ammonia production rises to a maximum and then declines. A large number of experiments conducted with nitrous oxide and ethylene at 900° C. showed that above this temperature pronounced polymerization and decomposition of the ethylene occurs.

According to Elöd and Nedelmann, the first stage in the process is the reduction of the nitric oxide to ammonia. Part of the ammonia then reacts with the hydrocarbon to form hydrocyanic acid (probably through the intermediary of unsaturated residues such as $:CH_2$ and $\vdots CH$), and the other part undergoes thermal dissociation to yield hydrogen and nitrogen. They saw very little probability of a reaction of ammonia directly with methane or solid carbon. The production of carbon monoxide may be accounted for by the reaction of ethylene with the water vapor formed in the reduction of nitric oxide. From these considerations it would appear that the process capable of giving best results would be the one starting with or favoring the initial formation of ethylene and ammonia.[145] Later results[146] have substantiated this, although the formation of acetylene seems a necessary condition for the production of hydrogen cyanide. Hydrocyanic acid is probably formed thus:[147]

$$2CO + NH_3 \longrightarrow HCN + CO_2 + H_2$$
$$CO_2 + H_2 \longrightarrow CO + H_2O$$

and by minor reactions involving the formation and decomposition of formaldehyde.

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[144] *Z. Elektrochem.*, 1927, **33**, 217; *Chem. Abs.*, 1927, **21**, 3254; *Brit. Chem. Abs.* **A**, 1927, 838.

[145] Bredig and Elöd use mixtures of ammonia and ethylene or acetylene in German Patent 548,798, 1927; *Chem. Abs.*, 1932, **26**, 4137.

[146] Bredig, Elöd and Demme, *Z. Elektrochem.*, 1930, **36**, 991; *Brit. Chem. Abs.* **A**, 1931, 176.

[147] Bredig, Elöd and Kortüm, *Z. Elektrochem.*, 1930, **36**, 1007. *Cf.* Bredig, Elöd and Müller, *ibid.*, 1930, **36**, 1003; *Brit. Chem. Abs.* **A**, 1931, 176.

Chapter 11

Direct Hydration of Olefins to Alcohols

The conversion of olefins to alcohols is normally effected by first combining the olefin with relatively concentrated sulphuric acid and subsequently hydrolyzing the alkylsulphuric acid initially formed. The same end may also be attained by using other acids in a more or less concentrated form (e.g., hydrochloric acid or hydrobromic acid) and hydrolyzing the resulting alkyl esters as before. It may be noted, however, that the conversion of olefins into alcohols merely involves the addition of the elements of water to the olefin according to the general scheme

$$C_nH_{2n} + H_2O \longrightarrow C_2H_{2n+1}OH$$

In this chapter the formation of monohydroxy alcohols by direct hydration is considered, and the subject of polyhydroxy alcohols (particularly glycols) is discussed in Chapter 22.

Direct hydration of higher olefins is known to take place with considerable ease under the influence of various chemical reagents, notably dilute mineral acids, but the direct hydration of the lower members of the series has been found to be considerably more difficult.[1] Thus, for example, the transformation of isobutylene into trimethylcarbinol can be accomplished, according to Butlerow,[2] in the cold in the presence of sulphuric acid of moderate dilution. Butlerow and Goriainow[3] found that amylene and heptylene, as well as isobutylene, can be hydrated to the corresponding alcohols at room temperature by means of 10 per cent nitric acid or 50 per cent sulphuric acid but on heating to 100° C. polymerization becomes the predominating reaction. Later, Miklaschewsky[4] observed that isobutylene and some of the amylenes and hexylenes can be hydrated by means of 5 to 10 per cent aqueous solutions of formic, acetic, or oxalic acids with no appreciable polymerization. Incidentally, a very interesting case of the hydration of a double bond has been reported by Solonina,[5] who obtained propylene glycol by refluxing allyl alcohol with 10 per cent by weight of hydrochloric acid. Michael and Brunel[6] carried out some experiments on the reaction of isobutylene with various concentrations of hydriodic acid and found that free alcohol and isobutylene iodide were formed in proportions depending upon the concentration of the hydriodic acid. When 60 per cent hydriodic acid was used the product consisted almost entirely of the iodide but with lower concentrations the products contained an increasing proportion of free alcohol. In the reaction of trimethylethylene with hydrobromic acid it was noted that acid stronger than

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[1] The hydration of olefins to alcohol might be designated as *aquolysis*, though strictly speaking this term is applied when water vapor is employed as a diluent at temperatures and pressures above the critical values (see Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, **1930**, 585).

[2] *Ann.*, 1867, **144**, 22.

[3] *Ann.*, 1873, **169**, 147; 1875, **180**, 245.

[4] *Ber.*, 1891, **24**, Ref. 269.

[5] *J. Russ. Phys.-Chem. Soc.*, 1887, **19**, 302; *Chem. Soc. Abs.*, 1888, **54**, 806.

[6] *Amer. Chem. J.*, 1912, **48**, 269.

9.66 normal yielded the bromide exclusively, while acid strengths lower than 5.54 normal produced only the alcohol. With acids of intermediate concentration, mixtures of the bromide and alcohol were obtained. Michael and Brunel concluded that in the hydration of these olefins by hydriodic or hydrobromic acids, the iodide or bromide was the intermediate compound which was subsequently hydrolyzed to the alcohol.

Brooks and Humphrey,[7] in the course of their well-known work on the action of sulphuric acid on olefins, came to the conclusion that practically complete hydration of some of the olefins can occur even with relatively dilute acids, as in the commercial process for the manufacture of terpineol. Similar results have been obtained with the amylenes and halogen acids.[8] Many examples of the hydration of double bonds to give alcohols are known in the paramenthane series, e.g., the hydration of sabinene by cold dilute sulphuric acid to yield terpineol-4. Of interest is the hydration of allene and dimethylallene to acetone and methyl isopropyl ketone by the distillation with steam of a solution of these gases in concentrated sulphuric acid.

Some of the processes in which the higher olefins are hydrated to alcohols under the influence of dilute mineral acids undoubtedly involve the intermediate formation of an ester which subsequently undergoes hydrolysis to an alcohol with liberation of the acid. In this way the hydrating acid perhaps acts as a catalyst. The lower olefins, which are very much more resistant to this method of hydration, usually require comparatively concentrated acids to effect absorption under ordinary conditions. Consequently the esters are usually the main products of the process and it is impossible to obtain alcohols exclusively.

Various procedures have been advanced in which the lower gaseous olefins, particularly ethylene, are heated under high pressure with dilute aqueous solutions of mineral acids or certain metallic salts at temperatures above 200° C., but the yields of alcohol obtained thereby have been very small. The general reaction

$$C_nH_{2n} + H_2O \rightleftharpoons C_nH_{2n+1}OH$$

is an equilibrium process since dehydration of alcohols yields olefins. There are also certain side reactions involving the formation of ethers. By the application of the third law of thermodynamics to this equilibrium process, Francis[9] deduced the following expression for the free energy of the synthesis of alcohols from olefins:

$$\Delta F = -5320 + 815n + 17.2T - 0.5nT,$$

in which n is the number of carbon atoms and T is the absolute temperature.

In the case of the lower olefins, this expression is positive for ordinary temperatures so that the tendency for alcohol formation from ethylene and water is small, i.e., at ordinary temperatures only relatively small amounts of alcohol would be in equilibrium with ethylene and water. Moreover, as the temperature is increased the expression for the free energy of formation becomes greater positively so that a rise in temperature should be unfavorable for alcohol production. On account of lack of reliable data it is almost impossible to apply the Nernst approximation formula to these equilibria. Since hydration takes place with a decrease in the number of molecules, increase of pressure should favor the formation of alcohols. Moreover, as may be inferred from the foregoing, low temperatures should favor the alcohol yields. However, as the reaction velocity is low at low temperatures, efficient catalysts are necessary for hydration under optimum conditions.

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[7] *J.A.C.S.*, 1918, **40**, 822.

[8] Butlerow, *Ann.*, 1877, **189**, 51; Wischnegradsky, *ibid.*, 1878, **190**, 351; Eltekow, *Ber.*, 1877, **10**, 707; Konowalow, *Ber.*, 1880, **13**, 2395.

[9] *Ind. Eng. Chem.*, 1928, **20**, 283; *Amer. Pet. Inst. Bull.*, 1930, III, 93.

Loveless and Wright[9a] calculated the relative values of the velocity and equilibrium constants over the temperature range of 0° to 500° C. They point out that the absolute values of these constants can be determined only if the integration constants can be evaluated. This requires a knowledge of the equilibrium proportions of ethylene, water and alcohol under one known set of conditions and the time required for the reaction to proceed to a measured extent. Thus far such data are not available. The free energy changes associated with the hydration of ethylene have been derived from the free energy data obtained by Francis,[9b] who gives the following equations:

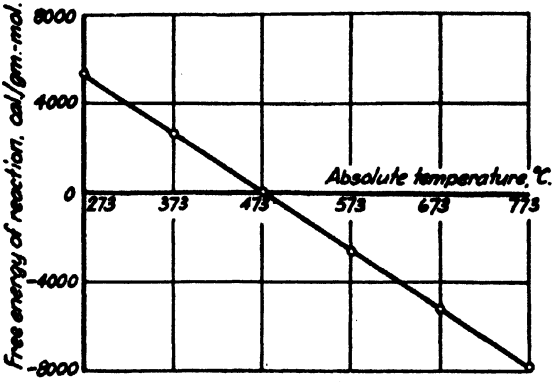
$$A_{C_2H_4} = 17{,}680 + 11.1T \ln T + 0.0055T^2 - 65T$$

$$A_{H_2O} = -57{,}410 + 0.94T \ln T + 0.00165T^2 - 0.00000037T^3 + 3.92T$$

$$A_{C_2H_5OH} = -50{,}520 + 20.33T \ln T - 0.0131T^2 - 85T$$

in which A is the change in free energy (calories per gram molecule) of formation of corresponding substances. For the hydration of ethylene in the vapor phase, the change in free energy is expressed by

$$\begin{aligned} A_{\text{Reaction}} &= A_{C_2H_4} + A_{H_2O} - A_{C_2H_5OH} \\ &= 10{,}790 - 8.29T \ln T + 23.92T + 0.00925T^2 - 0.00000037T^3 \end{aligned}$$



Courtesy Journal of the Royal Technical College (Glasgow).

FIG. 20.—Change in Free Energy of Reaction of Ethylene and Water with Temperature. (Loveless and Wright.)

This change in free energy plotted against the temperature over the range 0° to 500° C. (Fig. 20) gives a straight line which can be represented by the equation

$$A_{\text{Reaction}} = 12{,}600 - 26.3T$$

The rate of formation of alcohol can be expressed by the equation

$$\frac{dx}{dt} = k_1 (a - x)(b - x) - k_2 x$$

[9a] *J. Roy. Tech. Coll. (Glasgow)*, 1933, 3, 65.
[9b] *Loc. cit.*

in which k_1 and k_2 are the velocity constants for the forward and reverse reactions, respectively, a and b are the initial concentrations of ethylene and water, respectively, and x is the concentration of alcohol after time t.

The variation of the constant k with the temperature is given by the equation

$$\frac{d \ln k_1}{dT} = \frac{A}{RT^2} = \frac{1}{R}\left(\frac{12{,}600}{T^2} - \frac{26.3}{T}\right)$$

which on integrating becomes

$$\ln k_1 = -\frac{1}{R}\left(\frac{12{,}600}{T} + 26.3 \ln T\right) + C_1$$

The values of $(\ln k_1 - C_1)$ over the temperature range are shown in Figure 21. This curve indicates that the optimum temperature for investigating the effect of pressure on the reacting system is 200° C.

Variation of the equilibrium constant with the temperature is shown by the equation

$$\frac{d \ln K}{dT} = -\frac{U}{RT^2}$$

in which U is the heat of reaction.

$$\begin{aligned} U &= A - T\frac{dA}{dT} \\ &= 12{,}600 - 26.3T + T26.3 \\ &= 12{,}600 \text{ calories per gram molecule} \end{aligned}$$

Substituting this value of U in the above equation

$$\frac{d \ln K}{dT} = -\frac{12{,}600}{RT^2}$$

which on integrating becomes

$$\ln K = \frac{12{,}600}{RT} + C_2$$

The calculated values of $(\ln K - C_2)$ over the same temperature range as that for the variation in velocity constant are shown in Figure 22.

Catalysts capable of being used for hydration processes include dilute mineral acids which possibly are active by virtue of the presence of (hydrated) hydrogen ions, assumed to be the catalytic agents in many hydrolytic reactions. More concentrated acids possess esterifying action and the resulting alkyl esters are simultaneously hydrolyzed to a greater or less extent depending upon the acid concentration. A number of difficultly reducible metallic oxides exert a profound catalytic effect on both hydrating and dehydrating reactions. Among these may be mentioned alumina, thoria, and zirconia. Phosphoric acid (and its anhydride) has long been known as a valuable agent for the dehydration of alcohols so that its activity in the hydration of olefins is to be expected. Certain metallic phosphates, notably cadmium metaphosphate and cerium metaphosphate, have been mentioned as powerful catalysts for the hydration of ethylene. The mode of action of these catalysts is still uncertain but the observation of Weber and Walton[10] that the catalytic activity of phosphoric acid in the dehydration of ethyl alcohol to ethylene at 210° to 250° C. is much increased by the addition of 1.5 to 2 per cent of copper oxide, copper sulphate, silver sulphate, or aluminum sulphate, suggests that the metals function as promoters in conjunction with phosphoric acid. In a similar way Sabatier found that the dehydrating action of sulphuric acid on ethyl alcohol is accelerated by the addition of silver salts but Joshua, Stanley and Dymock[11] have employed sulphuric acid and silver sulphate on pumice as a catalyst for the vapor phase hydration of olefins. It appears therefore that the dehydrating and hydrating activity of both phosphoric and sulphuric acids is enhanced by the presence of certain of their metallic salts. In the case where a gaseous olefin is being forced to react with an aqueous liquid, any influence tending to increase the olefin concentration in the liquid phase is calculated to accelerate the reaction. For this reason certain metallic salts (e.g., silver, cuprous, and mercury salts) having a strong affinity for olefins have been proposed as catalysts for the hydration of olefins in the presence of liquid water.

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[10] *J. Phys. Chem.*, 1930, 34, 2693; *Ind. Chim.*, 1931, 327.

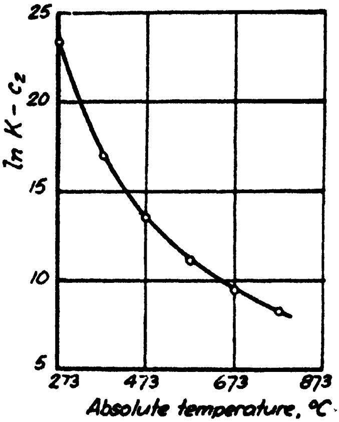

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FIG. 21.—Variation of Equilibrium Constant of Reaction of Ethylene and Water with Temperature. (Loveless and Wright.)

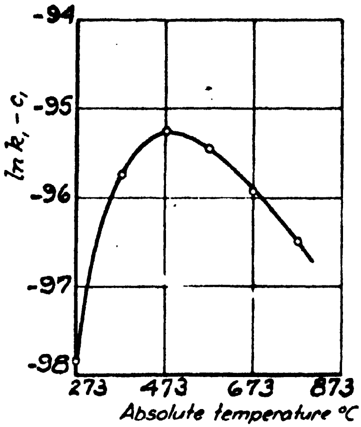

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FIG. 22.—Variation of Reaction Constant of Ethylene and Water with Temperature. (Loveless and Wright.)

ETHYLENE

Ethyl alcohol can be dehydrated to yield ethylene and water by warming with sulphuric or phosphoric acid, or, in the vapor phase, by heating in the presence of difficultly reducible oxide catalysts, such as alumina. The reverse reaction, or the hydration of ethylene to ethyl alcohol, was probably first shown by Cotelle.[12] The method used by him consisted in passing a mixture of steam and ethylene through a reaction tower countercurrent to a hot stream of dilute (10 to 12 per cent) sulphuric acid. Hot acid solution was withdrawn from the base of the tower, while alcohol and water vapors, together with unreacted ethylene, escaped at the top.

Another demonstration of the reversibility of the reaction

$$C_2H_5OH \rightleftharpoons C_2H_4 + H_2O$$

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[11] British Patent 370,136, 1931; assigned to The Distillers Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 716.
[12] U. S. Patent 41,685, Feb. 23, 1861.

was advanced by Wibaut and Diekmann,[13] who found when a mixture of ethylene and steam was passed over alumina, or aluminum sulphate, at 300° to 400° C., the reaction products contained 0.2 to 0.4 per cent of acetaldehyde. That this was not due to the oxidation of the ethylene was shown by passing a mixture of air and ethylene over the same catalysts at 360° C., when no acetaldehyde was formed, and hence the first step must have been the addition of water to the double bond, forming alcohol. In studying the action of an acid catalyst, the same investigators passed ethylene at ordinary pressure countercurrent to a descending stream of 65 per cent sulphuric acid at 156°-160° C. When passed at a rate of about 1 liter of ethylene per hour, approximately 5 per cent conversion to alcohol took place. Practically no conversion resulted with 55 per cent sulphuric acid.

When the general equation of Francis is applied to the equilibrium $C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$, the free energy of the alcohol synthesis reduces to

$$\Delta F = -3690 + 16.2T.$$

This expression is positive even at ordinary temperatures and increases (positively) with rising temperature. This indicates that the tendency for the reaction yielding alcohol to proceed would be small even at ordinary temperatures and would decrease at higher temperatures. The best conditions for the synthesis of alcohol from ethylene and water would therefore be:

(1) High pressures;
(2) Low temperatures consistent with sufficient velocity of reaction; and
(3) Highly efficient catalysts to bring about equilibrium quickly.

So far no catalyst has been discovered capable of inducing the reaction with sufficient speed at ordinary temperatures.

Klever and Glaser[14] recorded an important series of experiments on the hydration of ethylene. At atmospheric pressure hydration in the presence of mineral acids at 100° C. is very slow, but the reaction velocity increases considerably at higher pressures and temperatures, although the absolute effect is very slight. After 17 hours at 150° C. and 190 atmospheres pressure, one mole of water had hydrated only 0.00011 mole of ethylene, while at 200° C. and 100 atmospheres 0.0008 mole of ethylene was hydrated per mole of water. Under the latter conditions the effect is very favorably influenced by the presence of sulphuric acid in a concentration of over 0.17 per cent and of hydrochloric acid over 0.005 per cent. At a concentration of 1.93 per cent HCl, the catalytic effect is so marked (at 200° C. and 100 atmospheres) that more than one mole of ethylene is hydrated per mole of HCl. The intermediate product in the reaction was considered to be ethyl chloride, which was subsequently hydrolyzed to ethyl alcohol.

Swann, Snow and Keyes[15] have reported some results obtained by the hydration of ethylene and propylene under pressures of 600 to 800 lbs. per square inch at temperatures up to 200° C. in the presence of dilute mineral acids and solutions of metallic salts. Practically no hydration occurred in the presence of water alone. Table 72 gives these investigators' results.

It will be seen from Table 72 that the results indicate that halogen acids and salts do actually function as catalysts, but that the equilibrium concentration of alcohol is very small, as predicted by theoretical considerations. Swann and his

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[13] *Proc. Acad. Sci. Amsterdam*, 1923, **26**, 321; *Chem. Abs.*, 1923, **17**, 3858.
[14] *Mitt. Chem. Inst. Tech. Hochschule Karlsruhe*, 1923, **1**, 1-10; *Chem. Abs.*, 1924, **18**, 1976.
[15] *Ind. Eng. Chem.*, 1930, **22**, 1048.

TABLE 72.—*Catalytic Hydration of Ethylene.*

Expt.	Pressure lb./sq. in.	Temp. ° C.	Duration Hours	Catalyst	Conc. of Alcohol % by Wt.
9	600	150	1	None	0.007
7	600	100	1	5% HCl	0.06
8	600	125	1	5% HCl	0.10
2	600	135	2	5% HCl	0.13
1	600	135	21	5% HCl	0.09
4	600	200	1	5% HCl	0.06
5	600	150	1	$HgCl_2$ + 5% HCl	0.03
6	600	150	1	$AgNO_3$	0.14
18	800	150	1	None	0.008
16	800	100	1	5% HCl	0.087
17	800	125	1	5% HCl	0.14
12	800	150	1	5% HCl	0.132
11	800	150	2	5% HCl	0.15
10	800	150	21	5% HCl	0.10
13	800	200	1	5% HCl	0.088
14	800	150	1	$HgCl_2$	0.045
15	800	150	1	$AgNO_3$	0.202

collaborators also carried out some experiments on the hydration of ethylene under pressure using more concentrated acids and their results are given in Table 73.

TABLE 73.—*Effect of Different Concentrations of Acid upon the Hydration of Ethylene.*

Pressure = 800 lb. per sq. in.
Temperature = 150° C.
Time of Expt. = 3 hours.
Charge of aqueous solution = 150 cc.

Expt.	Catalyst	Conc. of Alcohol % by Wt.	Yield of Alkyl Halide Grams
25	None	0.0065	—
27	5% HCl	0.034	—
29	10% HCl	0.0867	—
30	15% HCl	0.083	—
31	20% HCl	0.052	—
32	25% HCl	0.063	—
33	25% HI	0.122	0.5
34	45% HI	0.141	24.0
35	35% HI	—	10.0
36	170 gm. 45% HI + 18 gm. conc. HCl	0.073	30.0
37	10% HCl + $AlCl_3$ (sat.)	0.0479	—
38	10% HCl + Cu_2Cl_2 (sat.)	0.0452	—
39	10% HCl + 1% $BiCl_3$	0.0335	—
40	10% HCl + 1% $HgCl_2$	0.061	—
41	20% HNO_3 + 1% $AgNO_3$	0.0043	—
42	40% HBr	0.0833	4.5
43	20% HBr	0.0842	—
44	11% HBr	0.0378	—

It will be seen that increasing the concentrations of the halogen acids favors the formation of the alkyl halide without greatly increasing the alcohol yields. With concentrated halogen acids, large quantities of the alkyl halide are formed.

Johannsen and Gross[16] advocated the direct hydration of ethylene by heating under pressure in the presence of water containing a small proportion of mineral acid. Temperatures of 200° C., pressures of not less than 20 atmospheres, and 4.3 per cent hydrochloric acid are recommended.

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[16] U. S. Patent 1,607,459, Nov. 16, 1926; *Chem. Abs.*, 1927, 21, 249. Also Röchlingsche Eisen- und Stahlwerke A.-G., British Patent 238,900, 1925; *J.S.C.I.*, 1925, 901B.

Smith and Bridger[17] described a process for producing ethyl alcohol from ethylene and water by hydration in the liquid phase under high pressure at temperatures of 200° to 300° C. in the presence of an inorganic salt having an affinity for ethylene (silver nitrate, cuprous chloride, and mercuric chloride) dissolved or suspended in water. A conversion of 10 per cent of the ethylene was obtained with a saturated aqueous solution of mercuric chloride in an autoclave protected by an internal coating of "Vitreosil."

Slade[18] proposed to hydrate ethylene to ethyl alcohol by passing it with excess of steam at 400° to 500° C. and 25 to 200 atmospheres over a dehydrating catalyst such as thoria, or phosphoric acid on pumice. The reaction is effected in the vapor phase and at a high space velocity (10,000 to 50,000 liters of gas at N.T.P. per hour per liter of catalyst). Heat interchange between the outgoing and incoming gases assists the reaction. The ethylene may be diluted with other gases and the process may be conducted in a continuous manner.

The vapor phase hydration of the lower olefins, including ethylene and propylene, is accomplished by passing them with steam at ordinary or increased pressures over certain catalysts at temperatures above 100° C. (usually about 150° to 300° C.). The catalysts proposed include finely divided metals of the platinum group, gold, silver, copper, iron, cobalt, nickel, chromium, tantalum, vanadium, tungsten, molybdenum or manganese, or their salts or other compounds.[19] These may be suspended on inert carriers or supports. This process is exemplified by the hydration of ethylene with steam over a catalyst of copper phosphate on pumice at 150° C. and atmospheric pressure. Hydration of ethylene or propylene takes place under similar conditions in the presence of catalysts consisting of copper oxide and tungstic oxide, of ferric oxide and tungstic oxide, or of finely divided platinum on pumice. In some instances appreciable proportions of the dehydrogenation products of alcohols (aldehydes and ketones) are obtained.

Direct hydration of ethylene with steam in the vapor phase may yield diethyl ether as the main product, small amounts of ethyl alcohol being simultaneously formed.[20] Conversion is effected by passing a gaseous mixture of steam and ethylene, with the latter in excess, under high pressure over various contact catalysts at temperatures below 300° C. and at moderate rates of gas flow (100 to 1000 liters of gas per hour per liter of catalyst). The catalysts may consist of non-volatile inorganic or organic acids or acid anhydrides (e.g., sulphuric acid, sulphonic acids, or better, phosphoric acid or phosphorus pentoxide) distributed on inert carriers. Phosphates of the rare earth metals, such as cerium metaphosphate, are particularly specified and the activity of the above catalysts is said to be improved by the addition of other substances, as, for example, zinc oxide or anhydrous zinc chloride. The amount of water vapor should not exceed 25 per cent by volume of the ethylene as otherwise marked formation of alcohol takes place. The following example illustrates this method: 24 liters of ethylene and 3 liters of water vapor (calculated under atmospheric pressure and at 20° C.) per hour are passed at 200° C. under a pressure of 125 atmospheres over 100 cc.

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[17] British Patent 308,468, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 426.

[18] British Patent 308,859, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 426.

[19] Bataafsche Petroleum Maatschappij, British Patent 335,551, 1930; *Brit. Chem. Abs.* **B**, 1931, 12; German Patent 569,019, 1930; *Chem. Abs.*, 1933, **27**, 2158; French Patent 695,849, 1930; *Chem. Abs.*, 1931, **25**, 2739.

[20] I. G. Farbenindustrie A.-G., British Patent 368,868, 1930; *Brit. Chem. Abs.* **B**, 1932, 636; French Patent 710,846, 1930; *Chem. Abs.*, 1932, **26**, 1614.

(apparent volume) of active carbon impregnated with a mixture of 11.25 grams of phosphorus pentoxide and 11.25 grams of phosphoric acid. About 7 cc. of ethyl ether and 0.5 cc. of ethyl alcohol are obtained per hour in one passage, corresponding to a 14 per cent yield of ether calculated on the ethylene employed.

Several processes developed by Joshua, Stanley, and Dymock deal with the direct vapor phase hydration of olefins to alcohols and particularly of ethylene to ethyl alcohol. Thus it is proposed[21] to hydrate ethylene to ethyl alcohol by passing it with steam at atmospheric or higher pressures and at temperatures of 140° to 200° C. over a contact mass of porous inert material (pumice) impregnated with about 60 per cent by weight of sulphuric acid, the concentration of the acid being maintained from about 60 per cent to 85 per cent by adjustment of the steam partial pressure. It is reported that by passing a mixture of 2 parts of ethylene and 1 part of steam at a gas rate of 180 liters per hour (calculated at normal temperature and pressure) over 3.6 liters (apparent volume) of the above catalysts at 170° C. and at a pressure of 15 atmospheres, a condensate was obtained containing 7.15 per cent of ethyl alcohol, representing a conversion of ethylene of 1.39 per cent.

Joshua, Stanley, and Dymock[22] further described the hydration of olefins to alcohols, with particular reference to ethylene, in the vapor phase in the presence of a catalyst of pumice (or other porous material) impregnated with about 60 per cent by weight of sulphuric acid together with a promoter, such as silver sulphate, known to accelerate the absorption of ethylene in concentrated sulphuric acid. For example, by passing a gaseous mixture of 1 part of ethylene and 1.5 parts of steam at a gas rate of 6.25 liters of the mixture per hour over a catalyst of 150 cc. (apparent volume) of pumice impregnated with 60 per cent by weight of sulphuric acid and 5 per cent by weight of silver sulphate at 145° C. and atmospheric pressure, a conversion of ethylene into ethyl alcohol of 1.6 per cent was obtained. The same investigators suggested[23] the hydration of olefins, particularly ethylene, to alcohols in the vapor phase by passing them with steam, most effectively under pressure, over certain acid sulphates (acid sodium sulphate or acid potassium sulphate) at temperatures not exceeding 350° C., particularly between 100° and 250° C.

Horsley[24] described a process for the direct vapor phase hydration of ethylene to ethyl alcohol under pressure in the presence of certain phosphate catalysts, notably a catalyst obtained by heating together cadmium oxide and phosphorus pentoxide in the molecular ratio of about 1:0.9. If the molecular proportion of phosphorus pentoxide falls below 0.725 the activity of the catalyst declines. Other catalysts (of somewhat lower activities than the cadmium phosphate) described by Horsley are the phosphates of beryllium, zinc, aluminum, tin, or lead. The reaction may be carried out either in the liquid or the vapor phase and at ordinary or increased pressure, the reaction temperature being preferably 100° to 300° C. To hydrate in the liquid phase, the olefin is compressed to, e.g., 100 atmospheres and passed through an aqueous solution of the catalyst salt to which has been added sufficient phosphoric acid to suppress hydrolysis. When operating in the vapor phase, it is best to employ a large excess of olefin relative to water vapor and the gaseous products are cooled to separate an aqueous alcohol solu-

[21] British Patent 368,051, 1931; assigned to The Distillers Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 590. See also French Patent 730,821, 1932; *Chem. Abs.*, 1933, 27, 305.

[22] British Patent 370,136, 1931; *Brit. Chem. Abs.* **B**, 1932, 716; French Patent 730,821, 1932; *Chem. Abs.*, 1932, 27, 305. Both patents assigned to The Distillers Co. Ltd.

[23] British Patent 368,935, 1931; assigned to The Distillers Co., Ltd.; *British Chem. Abs.* **B**, 1932, 670.

[24] British Patent 369,216, 1931; *Brit. Chem. Abs.* **B**, 1932, 670; German Patent 548,281, 1931; *Chem. Abs.*, 1932, 26, 3521. Both patents assigned to Imperial Chemical Industries, Ltd.

tion, the surplus ethylene being recirculated. This procedure is exemplified in the following: A catalyst was prepared by heating one mole of cadmium oxide and 1.5 moles of phosphoric acid in aqueous solution, the mixture being evaporated to dryness at a temperature below 130° C. and the product made into small pellets. A mixture of ethylene and steam under a total pressure of 100 atmospheres, the partial pressures of steam and ethylene being 30 and 70 atmospheres respectively, was passed over this catalyst at 290° C. with a contact time of about 1 minute. The products were said to consist of 243 grams of ethyl alcohol and 1.0 gram of ethyl ether per hour, together with 6.9 grams per hour of oily polymerization products. The yield of alcohol on the ethylene consumed was 95 per cent with a conversion per single passage of 3.36 per cent of the theoretical.

Later, Horsley[25] proposed to remove propylene from crude ethylene, which is to be used in the above hydration process, by polymerizing the propylene in the presence of the cadmium phosphate catalyst under conditions which leave the ethylene unchanged. It is probable therefore that the use of such catalysts in the hydration of the homologues of ethylene would be accompanied by the occurrence of polymerization reactions.

Phosphate catalysts, particularly those of uranium, iron and cobalt are employed by Joshua, Stanley and Dymock.[26] The proportion of phosphoric acid in the catalyst is in excess of that required for the orthophosphate of the metal used, but should not exceed 95 per cent of the composition of the finished material. Reaction between ethylene and water in the presence of these catalysts is carried out at temperatures of 100° to 300° C. (best above 150° C.) and at pressures up to 250 atmospheres. Some results obtained at atmospheric pressure with a number of iron catalysts (made by decomposing ferrous oxalate with phosphoric acid and drying at 200° C.) are given in Table 74. The percentage conversion of ethylene to ethyl alcohol was determined under fixed conditions, i.e., a gas rate of 3.12 liters of ethylene per hour per 100 cc. (apparent volume) of catalyst, an ethylene-steam ratio of 1 : 1.5 (by volume), and a catalyst temperature of 200° C., and also under variable conditions.

TABLE 74.—*Hydration of Ethylene with Iron Catalysts.*

Catalyst	Temperature ° C.	Pressure in Atmospheres	$C_2H_4:H_2O$ Molar Ratio	Liters of Ethylene per Hour per 100 cc. of Catalyst	Percentage Conversion of Ethylene to Ethyl Alcohol
$FeO \cdot 2H_3PO_4$	200	1	1:1.5	3.12	0.41
$FeO \cdot 2.5H_3PO_4$	200	1	1:1.5	3.12	0.69
$FeO \cdot 2.7H_3PO_4$	200	1	1:1.5	3.12	0.56
$FeO \cdot 3H_3PO_4$	200	1	1:1.5	3.12	0.40
$FeO \cdot 2.5H_3PO_4$	270	20	4:1	400	0.83
$FeO \cdot 2.5H_3PO_4$	280	40	7:1	1260	0.67

Catalysts prepared in a similar manner from cobaltous or uranyl oxalate were not as effective as the iron phosphates.

Manganese or copper phosphates (containing excess phosphoric acid) are recommended also.[27] For example, when ethylene and steam (in the molar ratio of 5.4: 1) are conducted over a copper phosphate catalyst (made from one mole of copper oxide and 2 moles of phosphoric acid) at 300° C., under a pressure of 40 atmospheres and at a gas rate of 1200 liters of ethylene per 100 cc. (apparent volume) of catalyst per hour, 22.1 grams of ethyl alcohol as a 14.5 per cent aqueous condensate is obtained. This corresponds to a 1.12 per cent conversion of ethylene.

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[25] British Patent 374,510, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 832.

[26] British Patent 392,289, 1932; assigned to The Distillers Co., Ltd.; *Brit. Chem. Abs.* **B**, 1933, 776.

[27] Joshua, Stanley and Dymock, British Patent 392,685, 1933; assigned to The Distillers Co., Ltd.

A study of the vapor phase hydration of ethylene at 360° to 380° C. at pressures of 70 to 135 atmospheres in the presence of alumina and tungstic oxide was conducted by Sanders and Dodge.[27a] Twenty-eight catalysts were prepared and tested by determinations of their efficiency in dehydrating ethyl alcohol to ethylene. Alumina and tungstic oxide (in one) were used in the hydration experiments, of which several results are given in Table 75.

TABLE 75.—*Hydration of Ethylene with Alumina Catalysts.*

Temp. ° C.	Pressure Atm.	Space Velocity [a]	Ethylene in Off-Gases Per Cent	Concentration of Ethanol in Product Per Cent by Wt.
364	70.9	480	97.3	1.79
363	90.1	430	95.4	2.44
359	78.5	710	96.3	1.40
362	71.1	695	97.6	1.41
359	70.2	240	97.7	1.53
360	69.6	93	96.9	1.83
362	67.5	145	84.7	2.05
361	69.6	110	95.6	2.59
360	69.6	120	96.4	2.39
378	69.6	86	94.7	2.97
380	69.6	47	71.0	2.04

[a] Liters of off-gas (at standard conditions) per hour per liter of catalyst.

Bent[28] has described the hydration of ethylene and its homologues by heating under high pressures in the presence of dilute aqueous solutions, or suspensions, of certain sulphates of heavy metals, zinc sulphate being specifically mentioned. The best results are obtained by bringing the olefin in contact in a continuous manner with an aqueous solution of zinc sulphate containing 8 to 25 per cent of $ZnSO_4.7H_2O$ (at 25° C.) at a temperature of 275° to 325° C. and a pressure from 175 to 250 atmospheres. Water is continually added to replace that carried forward as steam and alcohol. Thus, ethylene is treated at a rate of 1 liter per minute[29] with 300 grams of an aqueous solution of zinc sulphate solution (containing 25 per cent of the hydrated salt) maintained at a temperature of 300° C. and under a pressure of 210 atmospheres. About 20 per cent of the ethylene is converted into ethyl alcohol. The excess ethylene, after separation of the alcohol vapors, is recirculated.

Boron phosphate, free from excess boric and phosphoric acids, has been suggested as a catalyst for the hydration of olefins in either the gaseous or liquid phase.[30] This catalyst is prepared by evaporating to dryness a mixture of boric acid (62 grams) and an aqueous solution of phosphoric acid (100 grams). The resultant boron phosphate is freed of excess phosphoric acid by heating to 400° C. in a current of steam until the condensate gives no acid reaction with bromthymol blue. Hydration is carried out under pressure and at temperatures of 150° to 300° C. Passage of a mixture of 70 volumes of ethylene and 30 volumes of steam over this catalyst, under a total pressure of 100 atmospheres, at 290° C., and at a space velocity of 6000 reciprocal hours, yielded 155 grams of alcohol per hour per liter (apparent volume) of catalyst. No oil was produced under these conditions.

[27a] *Ind. Eng. Chem.*, 1934, 26, 208.

[28] British Patent 378,764, 1931; assigned to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1932, 1071. See also French Patent 729,765, 1931; *Chem. Abs.*, 1933, 27, 305.

[29] It is not specified whether this gas volume is measured at N.T.P. (the usual practice) or under the working pressure. On the former basis, the alcohol output per hour per liter of catalyst would be about 82 grams.

[30] Horsley, British Patent 378,865, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1932, 1071. See also Imperial Chemical Industries, Ltd., French Patent 734,989, 1932; *Chem. Abs.*, 1933, 27, 992.

The use of boron phosphate containing at least 10 per cent excess phosphoric acid over that required for the orthophosphate is advocated by Joshua, Stanley and Dymock.[31] Such a material is made by evaporating to dryness a mixture of one mole of boric acid anhydride and 2.2 moles of phosphoric acid, and heating the residue to 200° C. Passage of ethylene and steam (molar ratio of 4:1) under 20 atmospheres pressure, at a temperature of 270° C., and a gas velocity of 400 liters per hour per 100 cc. (apparent volume) of catalyst, yielded 3.70 grams of alcohol (per hour) as a 5.6 per cent aqueous condensate. This was equivalent to 0.44 per cent conversion of ethylene to ethyl alcohol.

Brown and Odell[32] described the hydration of olefin hydrocarbons to alcohols and ethers by passage with steam under pressure over catalysts (e.g., the oxides of aluminum, thorium, titanium, tungsten and chromium) at temperatures of 100° to 600° C. The relative proportions of alcohols and ethers formed are controlled by varying the temperature and the ratio of steam to olefin in the reacting gases. Generally, high temperatures and an excess of steam favor alcohol formation. In hydrating ethylene homologues somewhat lower temperatures are employed than with ethylene.

Dreyfus[33] effected direct hydration of olefins, particularly of ethylene to ethyl alcohol, by passage with steam (10 to 20 moles of olefin to 1 mole of steam) under pressure through heated liquid catalysts consisting of aqueous sulphuric, phosphoric, or sulphonic acids. When hydrating ethylene, the concentration of the sulphuric acid should be maintained at about 55 to 65 per cent, while concentrations of phosphoric acid of at least 85 per cent are necessary. As an illustration of this process, a mixture of ethylene and steam (in the molar proportions of 18 to 1) is conducted under a pressure of 50 atmospheres through aqueous sulphuric acid of about 75 per cent concentration at 165° C. and at a space velocity of 8000 liters per hour (calculated at N.T.P.) per liter of catalyst. The acid concentration falls to a steady value of 60 to 63 per cent. When using phosphoric acid, a higher temperature range (200° to 300° C.) is employed.

Dreyfus[34] also proposed to hydrate olefins in the presence of mineral acids of 60 to 90 per cent concentration (sulphuric and phosphoric acids) under pressure and at temperatures of 100° to 350° C. To these acids is added 2 to 40 per cent of the sulphuric or phosphoric esters of glycols, polyvalent alcohols (glycerol) and of higher fatty acids. Substances which aid the absorption of olefins in acids, such as lead or silver sulphate, may also be present in the catalyst liquid. A mixture of ethylene and propylene is hydrated, for example, in the presence of 70 per cent sulphuric acid containing 15 per cent of aromatic sulphostearic acids and about 5 per cent of hydroxystearylsulphuric acid, all maintained at 180° C.

A modification[35] of the above processes involves the use of dilute solutions of mineral acids. Concentrations of acid varying from 2 to 10 per cent are

[31] British Patent 396,724, 1933; assigned to The Distillers Co., Ltd.

[32] U. S. Patents 1,873,536 and 1,873,538, Aug. 23, 1932; *Chem. Abs.*, 1932, 26, 5962, 5963. In this latter patent saturated hydrocarbons are used as starting materials, being cracked to olefins.

[33] British Patent 389,133, 1931; *Brit. Chem. Abs.* B, 1933, 457; also French Patent 741,068, 1932; *Chem. Abs.* 1933, 27, 2691.

[34] French Patent 744,164, 1933; *Chem. Abs.*, 1933, 27, 3942.

[35] Dreyfus, French Patent 744,482, 1933; *Chem. Abs.*, 1933, 27, 3942.

recommended, though concentrations as high as 50 per cent may be employed. Thus, a mixture of 3 volumes of ethylene and 2 volumes of steam, preheated to 150° C., is led through 10 per cent sulphuric acid at 200° C. under a pressure of 25 atmospheres. The time of contact is about 30 seconds.

Dreyfus[36] also proposed to effect the hydration of olefins, particularly ethylene, in the presence of certain acid salts having an affinity for water. Such salts include bisulphates, pyrosulphates, particularly those of the alkali metals, calcium chloride, zinc chloride and magnesium chloride. A mixture of steam with at least an equal molar proportion of the olefin is passed under pressures up to 25 atmospheres over these catalysts at 150° to 350° C.

The alkali hydroxides and other basic substances have been suggested as catalysts for direct hydration, especially at temperatures of 150° to 250° C. and under pressures of 50 atmospheres or higher.[37] Calcium or magnesium oxide may be employed as catalysts, either alone or in conjunction with alkali hydroxides. The passage of equal volumes of ethylene and steam through a 50 per cent potassium hydroxide solution at 150° C. under 20 atmospheres pressure and also the use of pumice impregnated with sodium hydroxide to catalyze a mixture of one volume of ethylene and two volumes of steam at 200° C. under 30 atmospheres pressure are examples of this process.

Other catalysts which have been suggested are liquid phosphoric acid[38] and the molten chlorides of metals at least as electropositive as nickel, e.g., calcium, zinc or magnesium chloride.[39]

Another procedure, which apparently combines both direct esterification and hydrolysis of the esters formed, consists in conducting (under pressure) steam, olefin and the vapors of aliphatic acids (e.g., acetic or trichloroacetic acid) over catalysts, such as zinc chloride, at temperatures of 150° to 600° C. The proportion of acid vapors should be small as compared with the olefin and steam present, so that only a small amount of esters is produced.[40]

A two-stage process is described by Dreyfus,[41] in which olefins are absorbed (under 50 to 100 atmospheres pressure and at temperature of 250° to 300° C.) in aqueous solutions of orthophosphoric acid, or of weaker acids. The products are subsequently hydrolyzed with water or steam. The concentration of the acid employed varies with the individual olefin, being about 80 per cent for ethylene, 75 per cent for propylene, and 60 per cent for higher olefins.

COMPARISON OF AVAILABLE DATA ON HYDRATION OF ETHYLENE

In the absence of any published systematic study of the relative efficiencies of various catalysts for the hydration of ethylene, the somewhat meager information available furnishes the only basis for such comparison. Unfortunately, however, this information is not always sufficient for an adequate assessment of the value of a process. From the viewpoint of the industrial application of the hydration reaction, the most rational basis of comparison would be the hourly output of alcohol per unit volume (apparent) of catalyst at a definite pressure and temperature. Table 76 contains the data available in this connection.

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[36] French Patent 745,084, 1933; *Chem. Abs.*, 1933, 27, 4239. See also Dreyfus, French Patent 745,042, 1933; *Chem. Abs.*, 1933, 27, 4239; British Patents 394,375 and 394,674, 1931; *Brit. Chem. Abs.* B, 1933, 855.

[37] Dreyfus, British Patent 389,133, 1931; *Brit. Chem. Abs.* B, 1933, 457; French Patent 742,512, 1933; *Chem. Abs.*, 1933, 27, 3481.

[38] Dreyfus, British Patent 394,389, 1931; *Brit. Chem. Abs.* B, 1933, 855.

[39] Dreyfus, British Patent 396,104, 1933.

[40] Dreyfus, British Patent 394,376, 1931; *Brit. Chem. Abs.* B, 1933, 855; French Patent 746,463, 1933; *Chem. Abs.*, 1933, 27, 4539.

[41] British Patent 394,187, 1932.

TABLE 76.—*Comparison of Alcohol Outputs.*

Reference	Catalyst	Pressure Atmos.	Temp. ° C.	$C_2H_4:H_2O$ Molar Ratio	Alcohol Output, Grams per Liter of Catalyst
a	$CdO \cdot 2H_3PO_4$	100	290	70:30	243
b	BPO_4	100	290	70:30	155
c	$ZnSO_4$ solution	210	300	—	82(?)
d	$FeO \cdot 2.5H_3PO_4$	20	270	16:4	67.8
d	$FeO \cdot 2.5H_3PO_4$	40	280	35:5	174
d	$CoO \cdot 2.5H_3PO_4$	20	270	16:4	31.8
d	1 (Uranyl oxalate) + $2.3H_3PO_4$	20	270	16:4	30.3
e	$MnO \cdot 2.7H_3PO_4$	20	250	15:5	38.0
e	$CuO \cdot 2H_3PO_4$	20	270	16:4	70.9
e	$CuO \cdot 2H_3PO_4$	40	300	34:6	221
f	$1B_2O_3 \cdot 2.2H_3PO_4$	20	270	16:4	37

[a] Horsley, British Patent 369,216, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 670.

[b] Horsley, British Patent 378,865, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 1071.

[c] Bent, British Patent 378,764, 1931; assigned to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1932, 1071.

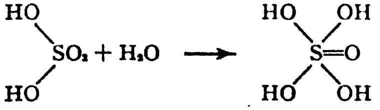
[d] Joshua, Stanley and Dymock, British Patent 392,289, 1932; assigned to The Distillers Co., Ltd.; *Brit. Chem. Abs.* **B**, 1933, 776.

[e] Joshua, Stanley and Dymock, British Patent 392,685, 1932; assigned to The Distillers Co., Ltd.; *Brit. Chem. Abs.* **B**, 1933, 776.

[f] Joshua, Stanley and Dymock, British Patent 396,724, 1933; assigned to The Distillers Co., Ltd.

PROPYLENE

Little work has been done on the direct hydration of propylene to isopropyl alcohol or on the direct hydration of butene-1 and butene-2. As pointed out previously the hydration of isobutylene, hexenes, and certain heptenes appears to take place very readily under the influence of moderately dilute mineral acids. The hydration of olefins by dilute mineral acids probably runs parallel, to some extent at any rate, with the tendency to form alkyl esters with more concentrated acids. Brooks and Humphrey[41a] concluded from their work that the tendency of aliphatic olefins to form alkylsulphuric esters and alcohols appeared to be at a maximum with the amylenes and hexylenes. It was also noted that when the simple olefins such as the amylenes, hexenes, or heptenes are carefully treated with 85 per cent sulphuric acid at a temperature not exceeding 15° C. and the resulting clear, amber-colored acid solution slowly poured into iced water, there is immediately precipitated a pale yellow oil containing as its chief constituent the free (secondary or tertiary) alcohol corresponding to the original hydrocarbon. To account for the fact that free alcohol was not present before dilution while the rates of hydrolysis of the alkylsulphuric esters concerned were far too low to admit of the degree of hydrolysis observed, Brooks and Humphrey assumed that the actual intermediate products were readily hydrolyzable alkyl esters of orthosulphuric acid, the latter being formed by the union of water and sulphuric acid according to the scheme:



[41a] *J.A.C.S.*, 1918, 40, 822. *Cf.* Michael and Brunel, *Amer. Chem. J.*, 1909, 41, 118.

Swann, Snow, and Keyes[41b] studied the direct hydration of propylene under 600 to 800 lbs. per square inch pressure at 135° C. in the presence of dilute hydrochloric acid and aqueous solutions of silver nitrate. Their results are recorded in Table 77.

TABLE 77.—*Hydration of Propylene.*

Expt.	Pressure Lbs./sq. in.	Temp. ° C.	Duration Hours	Catalyst	Conc. of Alcohol Wt. %
19	600	135	1	5% HCl	0.44
20	600	135	1	$AgNO_3$	0.22
21	800	135	1	5% HCl	0.63
22	800	135	1	$AgNO_3$	0.32
23	800	135	1	$AgNO_3$	0.29

It will be seen from the above figures that though the extent of hydration of propylene is several times greater than that of ethylene under similar conditions, the effect is still very minute. The application of the general formula of Francis for the free energy of formation of alcohols from olefins and water to propylene leads to the following expression:

$$\Delta F = -2875 + 15.7T.$$

This is no more promising from the point of view of the synthesis of isopropyl alcohol from propylene than is that for the production of ethyl alcohol from ethylene. On the other hand, it is stated that propylene and higher olefins may be catalytically hydrated to secondary and tertiary alcohols in such a way that propylene and its higher homologues may be removed from mixtures with ethylene, which is itself largely unchanged under the conditions employed.[41c] This would indicate that propylene and its homologues are much less resistant to catalytic hydration than is ethylene. In this process, propylene and its immediate higher homologues are allowed to react with a dilute acid, or aqueous salt solution having an acid reaction, in the presence of a catalyst at 100° to 250° C. (preferably 150° to 220° C.) and at a partial pressure of the olefin gas not less than 10 atmospheres. Catalysts specified are bismuth chloride, bismuth oxychloride, cuprous chloride, copper sulphate, copper phosphate, copper toluene-p-sulphonate, copper naphthalene disulphonate, silver sulphate, and silver naphthalene disulphonate. As dilute acids, hydrochloric, sulphuric, or phosphoric acids, or organic sulphonic acids such as toluene-p-sulphonic and naphthalene disulphonic acids, may be employed.

McKee and Burke[41d] recommended a procedure for the manufacture of higher (secondary and tertiary) alcohols from ethylene homologues by vapor phase hydration, using a mixture of steam and the olefin at temperatures of 350° to 450° C. and pressure of 25 to 200 atmospheres in the presence of dehydrating oxide catalysts, such as alumina, thoria, or zirconia.

In a process[42] which has been previously discussed, the direct vapor phase hydration of propylene is proposed in the presence of catalysts consisting of certain finely divided metals of the platinum group, or gold, silver, copper, iron, cobalt, nickel, chromium, tantalum, vanadium, tungsten, molybdenum, or manganese, or salts or compounds thereof, at temperatures above 100° C. (best at 150° to 300° C.) and even at atmospheric pressure. A mixture of copper oxide and tungstic acid is mentioned as particularly applicable for the hydration of propylene. A mixture of propylene and water vapor is conducted at a velocity of 6.7 cc. per hour (per cubic centimeter of apparent catalyst volume) over a catalyst, made by depositing 15 grams of cupric oxide and 15 grams of tungsten trioxide on 150 grams of active carbon. The aqueous condensate obtained at a reaction temperature of 300° C. is reported to contain alcoholic bodies.

[41b] *Ind. Eng. Chem.*, 1930, **22**, 1048.

[41c] I. G. Farbenindustrie A.-G., British Patent 324,897, 1928; *Brit. Chem. Abs.* **B**, 1930, 408.

[41d] U. S. Patent 1,738,785, Dec. 10, 1929; *Chem. Abs.*, 1930, **24**, 955.

[42] Bataafsche Petroleum Maatschappij, British Patent 335,551, 1930; *Brit. Chem. Abs.* **B**, 1931, 12.

Bent[43] has suggested the direct hydration of propylene to isopropyl alcohol by heating under high pressure in the presence of aqueous solutions of sulphates. Propylene is introduced at a rate of about 7 liters per minute into a pressure vessel containing 650 grams of an aqueous solution of zinc sulphate (8 per cent $ZnSO_4.7H_2O$ at 25° C.) at a temperature of 286° C. and a total pressure of 210 atmospheres. Isopropyl alcohol, water and unused propylene are continuously withdrawn from the top of the container and water is fed in to maintain the concentration of the aqueous solution.

Boron phosphate is a catalyst for the vapor phase hydration of propylene.[44] On passing a mixture of equal volumes of steam and propylene at a space velocity of 1000 reciprocal hours over this catalyst at 200° C. at atmospheric pressure, a condensate was obtained which contained 1 per cent by weight of isopropyl alcohol, corresponding to a yield of 98-99 per cent of the propylene reacting. This represents a conversion of propylene per passage of about 0.3 per cent at a time of contact of 3.6 seconds. About the same degree of conversion is secured with ethylene under similar conditions of steam to olefin ratio, temperature, pressure, and space velocity in the presence of cadmium (acid) phosphate.[45]

In the process of Suida,[46] the higher homologues of ethylene are said to be converted into a mixture of the corresponding alcohols and their esters by causing such olefins to react with dilute aliphatic acids in the presence of not more than 5 per cent of a strong mineral acid under pressure at temperatures above 100° C. For example, propylene is absorbed in a 15 per cent aqueous acetic acid solution containing 3 per cent of concentrated sulphuric acid at 150° C. under 20 atmospheres pressure to yield a product consisting of isopropyl alcohol and isopropyl acetate in the proportion of 8:1.

ISOBUTYLENE

As previously indicated, isobutylene in conjunction with certain other branched chain olefins can be slowly hydrated even in the presence of 5 to 10 per cent aqueous solutions of weak organic acids without appreciable polymerization. The hydration of these hydrocarbons in the presence of such feeble catalysts is too slow, however, for commercial purposes. Owing to the pronounced tendency of isobutylene to polymerize in the presence of strong acids, even at low tempera-

TABLE 78.—*Equilibrium Constants of the Reaction*

$$\text{iso-}C_4H_8 + H_2O \rightleftharpoons \text{ter-}C_4H_9OH.$$

Temp. ° C.	Temp. ° Absolute	*K*
80	353	1.25
167	440	0.021

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[43] British Patent 378,764, 1931; assigned to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1932, 1071.

[44] Horsley, British Patent 378,865, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 1071.

[45] Horsley, British Patent 369,216, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 670.

[46] U. S. Patent 1,836,135, Dec. 15, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 994.

tures, attempts to hydrate this olefin and similar reactive olefins in the presence of the known active hydrating catalysts would undoubtedly lead to the formation of relatively large proportions of polymerized substances. Francis[47] gave the figures in Table 78 for the equilibrium constants of the reaction between isobutylene, water, and tertiary butyl alcohol at two temperatures.

The figures in Table 78 show that the tendency for isobutylene to react with water to form tertiary butyl alcohol falls off very rapidly with rising temperature, although at the lower temperature (80° C.) quite high conversions of isobutylene into the corresponding alcohol are theoretically possible.

BUTENE-2

A study of the hydration of butene-2 to butanol-2 in the vapor phase under high pressure has been contributed by Marek and Flege.[48] The catalysts employed were cuprous chloride, phosphoric acid, copper phosphate and thoria at temperatures of 427° to 538° C. The pressures were 3000 and 5000 pounds per square inch (211 and 352 kg. per sq. cm., respectively). Under these conditions the hydration reaction was accompanied by polymerization, to avoid which a large excess of steam over butene was employed. The yield of polymerized products was reduced by increasing the steam-butene ratio and increased by the use of higher pressures and temperatures. All the catalysts were effective in speeding up hydration reactions but exerted little effect on polymerization. This is shown by the data in Table 79, all of which refer to experiments at a pressure of 3000 pounds per square inch using a reaction mixture consisting of 50 moles of steam to 1 mole of butene.

TABLE 79.—*Effect of Temperature and Catalysts on Hydration.*

(Pressure 3000 lb. per sq. in., or 211 kg. per sq. cm.;
mole ratio of steam to butene-2, 50 to 1)

Catalyst	Temp. ° C.	Time of Contact Sec.	Butene-2 To Products Hydrated	Butene-2 To Products Polymerized	Conc. of Hydrated Products in Exit Aqueous Solution
			Per Cent	Per Cent	Per Cent
Cu_2Cl_2	427	77	6.4	0.00	0.50
Cu_2Cl_2	427	78	6.3	<0.05	0.51
Cu_2Cl_2	482	70	6.8	0.50	0.58
Cu_2Cl_2	482	72	6.8	0.30	0.58
Cu_2Cl_2	538	65	—	4.20	0.06
None	427	78	0.46	0.00	0.03
None	482	72	2.16	0.00	0.22
None	538	68	4.90	2.30	0.38
$Cu_3(PO_4)_2$	427	74	3.52	<0.05	0.28
$Cu_3(PO_4)_2$	482	69	4.50	<0.05	0.34
$Cu_3(PO_4)_2$	538	64	5.00	5.00	0.44
Thoria	427	71	2.4	<0.05	0.18
Thoria	482	67	5.2	0.72	0.53
Thoria	538	63	7.7	6.80	0.62

The results of a series of experiments with varying times of contact and mole ratio of reactants are given in Table 80.

An inspection of the results in Table 80 shows that an increase in the proportion of steam favors hydration but lowers the concentration of hydrated

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[47] Francis and Kleinschmidt, *Amer. Pet. Inst. Bull.*, 1930, III, 93; *Chem. Abs.*, 1930, 24, 2369.
[48] *Ind. Eng. Chem.*, 1932, 24, 1428.

TABLE 80.—*Effect of Mole Ratio and Time of Contact on Hydration.*

(Pressure, 3000 lb. per sq. in. or 211 kg. per sq. cm.)

Catalyst	Temp. ° C.	Mole Ratio $H_2O:C_4H_8$	Time of Contact Sec.	Butene-2 To Products Hydrated	Butene-2 To Products Polymerized	Conc. of Hydrated Product in Exit Aqueous Solution
				Per Cent		
Cu_2Cl_2	427	50.0	78	6.3	<0.05	0.51
Cu_2Cl_2	427	10.0	78	1.24	0.16	0.50
Cu_2Cl_2	427	1.0	71	0.3	1.5	1.00
Cu_2Cl_2	482	10.0	72	2.7	0.31	1.10
Cu_2Cl_2	482	1.0	67	1.01	1.48	1.86
Cu_2Cl_2	482	1.0	137	0.88	8.5	3.60
Thoria	427	50.0	71	2.44	<0.05	0.18
Thoria	427	10.0	67	0.83	<0.05	0.31
Thoria	482	50.0	67	5.2	0.72	0.53
H_3PO_4	427	10.0	65	3.6	0.0	1.40
H_3PO_4	427	10.0	364	3.2	<0.05	1.21
H_3PO_4	482	10.0	59	4.4	<0.05	1.57
H_3PO_4	482	10.0	310	1.91	24.1	0.70
H_3PO_4	538	10.0	138	1.87	27.8	0.57
H_3PO_4	538	10.0	57	5.4	<0.05	2.07

products in the condensate. Under comparable conditions, the amount of olefin hydrated relative to that polymerized was greatest with the phosphoric acid catalyst. An increase in the time of contact from 65 to 364 seconds in the presence of phosphoric acid at 427° C. varied the percentage hydration of butene-2 to only a slight degree, indicating that equilibrium was approached under these conditions. At higher temperatures, however, an increase in the contact time resulted in diminished yields of hydrated products and an increase in polymerization.

The experiments in Table 81 on the influence of pressure in the presence of various catalysts, show that an increase of pressure from 3000 to 5000 pounds per square inch favored polymerization to a much greater extent than hydration.

TABLE 81.—*Effect of Pressure on Hydration.*

(Mole ratio of steam to butene-2, 50 to 1)

Catalyst	Temp. ° C.	Pressure Lbs. per sq. in.	Time of Contact Sec.	Butene-2 To Products Hydrated	Butene-2 To Products Polymerized	Conc. of Hydrated Product in Exit Aqueous Solution
				Per Cent		
Cu_2Cl_2	427	5000	132	7.6	1.10	0.60
Cu_2Cl_2	427	3000	77	6.4	0.00	0.50
Cu_2Cl_2	482	5000	122	3.1	2.10	0.24
Cu_2Cl_2	482	3000	72	6.8	0.3	0.58
Thoria	427	5000	132	2.3	4.4	0.11
Thoria	427	3000	76	2.40	<0.05	0.18
Thoria	471	5000	121	4.70	1.60	0.37
Thoria	465	3000	67	5.2	0.72	0.53

Under conditions where polymerization was reduced to a negligible amount, the conversion of butene-2 into hydrated products was only about 3 to 6 per cent per passage even under such high pressures as 3000 pounds per square inch (210 atmospheres). Marek and Flege, however, employed much higher temperatures than are usually considered desirable and accordingly a large excess of steam over butene was necessary to suppress polymerization. By using more active catalysts at lower temperatures it should be possible to employ lower steam-olefin ratios without the occurrence of extensive polymerization. A further disadvantage of temperatures as high as 400° to 500° C. is that under such conditions the alcohols tend to become dehydrogenated, yielding ketones and their condensation products.[49] Accordingly purer alcohols would probably be obtained by conducting hydration at lower temperatures in the absence of catalysts capable of catalyzing dehydrogenation.

The hydration of butenes by heating with aqueous solutions, or suspensions, of the heavy metals sulphates, particularly zinc sulphate, has been suggested by Bent.[50] Temperatures of 200° to 375° C. and pressures not less than 100 atmospheres are recommended.

SUMMARY AND CONCLUSIONS

The general reaction

$$C_nH_{2n} + H_2O \rightleftharpoons C_nH_{2n+1}OH$$

is reversible and represents both the direct hydration of olefins to alcohols and the dehydration of alcohols to olefins. While some of the higher olefins, such as amylenes, hexenes or isobutylene, appear to be hydrated fairly readily by moderately dilute mineral acids, the simple gaseous olefins, ethylene and propylene, are much more resistant to direct hydration. The thermodynamic calculations indicate that comparatively low temperatures are necessary to obtain appreciable quantities of alcohols and that efficient catalysts and high pressures are required. Even at low temperatures the equilibria are well over to the olefin side of the equation, i.e., the equilibrium concentrations of alcohol are small.[50a]

From the calculated free energies of the formation of alcohols, up to and including hexanol, Frost[51] concluded that high pressures and temperatures of 227° to 427° C. favor the direct hydration of olefins.

In spite of these adverse considerations much work has been done with a view to perfecting processes for the alluring reaction of direct hydration of the lower olefins. It cannot be said, however, that these efforts have been crowned with anything in the nature of success. Doubtless the seeming simplicity of the reaction will continue to entice that type of investigator who possesses the confidence that success lies just around the corner.

On the other hand, from details given in the process[52] of the I. G. Farbenindustrie already noted, it appears that propylene is somewhat more amenable to the hydration process than is ethylene.

Very much more promising than the direct hydration of ethylene and propylene appears to be the use of acids of catalytic strength, i.e., of a strength exceeding that necessary for the direct hydration process but yielding, on combination with gaseous olefins under pressure, not only free alcohols but also alkyl esters of the mineral acid. Thus, for example, Swann, Snow and Keyes[53] in discussing the results obtained by heating ethylene under 800 lbs. per square inch pressure in the presence of halogen acids of higher ranges of concentration, state:

"Increasing the concentration of hydrobromic or hydriodic acids favors the formation of the alkyl halide without apparently increasing the alcohol formation. With the concentrated acid, large proportions of the alkyl halide are formed. Since the halides are so easily obtained in large quantities and since they may be rather easily hydrolyzed photochemically or catalytically, an indirect process (of making alcohol) may be developed involving the steps: formation of alkyl halide, hydrolysis of halide, and reconcentration of acid." It is difficult to see, however, in what way such a process will offer advantages over the sulphuric acid process, particularly as halogen acids are difficult to reconcentrate in bulk.

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[49] The butanol-2 obtained by Marek and Flege showed an acetylation value corresponding to about 81.5 per cent butanol.

[50] British Patent 378,764, 1932; assigned to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1932, 1071.

[50a] *Cf.* Sanders and Dodge, *Ind. Eng. Chem.*, 1934, 26, 208.

[51] *Zhur. Prikladnoi Khim.*, 1930, 3, 1069; *Chem. Abs.*, 1931, 25, 3233.

[52] British Patent 324,897, 1928; *Brit. Chem. Abs.* B, 1930, 408.

[53] *Loc. cit.*

Closely related is the proposal advanced by McElroy[54] to manufacture alcohols by passing a current of gaseous olefins (propylene especially) upwards in intimate contact with a downwardly moving current of hot dilute acid (of catalytic hydrating strength), removing alcohol vapors, water vapor and residual gas after such contact, removing concentrated acid liquor at the bottom, and subsequently returning the acid to the top of the tower after adding to it sufficient water to compensate for that used up in the hydration process. Such a process might be considered to occupy a position midway between the direct hydration process and the ordinary concentrated sulphuric acid process. The alkylsulphuric esters are hydrolyzed by dilution with water, the alcohols distilled off, and the acid reconcentrated to its original esterifying strength for further use.

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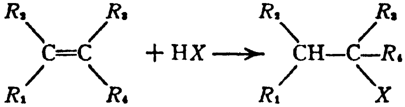
[54] U. S. Patent 1,438,123, Dec. 5, 1922; *J.S.C.I.*, 1923, 42, 119A. *Cf.* Cotelle. U. S. Patent 41,685, Feb. 23, 1861.

Chapter 12

Direct Esterification of Olefins with Mineral and Organic Acids

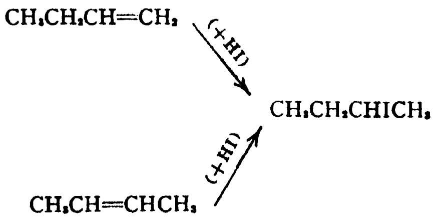
Many instances are known of the direct combination of olefins with mineral and other acids to yield esters of alcohols, and evidence of many more is being rapidly accumulated. The subject is of very great importance since the normal procedure for the manufacture of alcohols from olefins includes the union of these compounds with sulphuric acid to produce alkylsulphuric esters. Moreover the possibility of directly esterifying olefins to yield certain desirable esters of the corresponding alcohols opens up a wide and promising field of research.

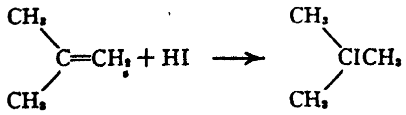
The reaction involved in the direct esterification of olefins may be expressed by the equation:



where R_1, R_2, R_3, and R_4 are aliphatic radicals or hydrogen, and X represents an acidic radical such as —Cl, or —SO_4H. Under the proper conditions, however, this reaction becomes a reversible one.

An important rule governing the addition of halogen acids to olefins is that proposed by Markownikov,[1] who stated that the halogen atom of the halogen acid tends to become united to the carbon atom which is combined with the least number of hydrogen atoms. Another way of stating this is that addition takes place in such a manner as to produce the maximum number of methyl groups in the molecule. Thus 1-butene and 2-butene add hydriodic acid with the production of the same secondary butyl iodide,[2] while isobutylene yields the tertiary iodide almost entirely.





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[1] *Ann.*, 1870, 153, 256. Also, Butlerow, *Ann.*, 1868, 145, 274.

[2] Lieben and Rossi, *Ann.*, 1871, 158, 166.

However, Ipatiev and his collaborators[3] found that when the higher ethylenic hydrocarbons are treated with a solution of hydrogen bromide in glacial acetic acid the combination does not take place normally according to Markownikov's rule as there is also found a certain amount of abnormal products. For various olefins the proportion of these products formed is different and becomes less with the increasing difference between the amounts of hydrogen united with the carbon atoms on either side of the double linking. Thus with isobutylene, containing the grouping $>C=CH_2$, the proportion of abnormal product is 6 to 7 per cent; with trimethylethylene, having $>C=CH—$, 10 to 15 per cent and with isopropylethylene, possessing $—CH=CH_2$, 50 per cent.

The work of Ipatiev has been confirmed and enlarged to a certain extent by Delacre.[4] The latter found that crude 3.3-dimethyl-1-butene and hydrogen bromide gave the primary bromide instead of the expected secondary derivative. It was thought that the impurities associated with the crude hydrocarbon exerted the same action as acetic acid, the solvent employed by Ipatiev.

According to Brunel[5] the equilibrium

$$\text{isobutyl bromide} \rightleftharpoons \text{tertiary butyl bromide}$$

is established at 280° C. when the mixture contains about 90 per cent of the tertiary bromide. Thus the reaction of halogen acids with isobutylene at high temperatures yields principally the tertiary product, though at lower temperatures somewhat more of the isobutyl bromide is obtained.

ETHYLENE

The direct combination of ethylene and sulphuric acid to yield the ethyl esters of sulphuric acid has long been known. The preparation of ethyl and of isopropyl alcohols from ethylene and from propylene, respectively, by the formation of the corresponding alkylsulphuric acid and subsequent hydrolysis, was investigated by Berthelot.[6] The absorption of the olefins by the acid did not take place under practical optimum conditions, however, and the yields of alcohols were insignificant.

The ethylene is normally absorbed in about 96 per cent sulphuric acid at a temperature not greatly exceeding 100° C. Plant and Sidgwick[7] later showed that besides ethylsulphuric acid some diethyl sulphate, $(C_2H_5)_2SO_4$, was formed, but not until the concentration of ethylsulphuric acid had attained a high figure. Still later, Damiens[8] observed that the yield of diethyl sulphate was higher at low temperatures and with concentrated (100%) sulphuric acid. Maimeri[9] found that if the absorption of pure ethylene in 100 per cent sulphuric acid was conducted under pressure it then became very rapid and much diethyl sulphate was formed at ordinary temperatures. Thus at 3.5 atmospheres pressure of ethylene (using 100% acid) the yield of diethyl sulphate was 35 per cent and of ethylsulphuric acid 51 per cent, based on the sulphuric acid, while at 10 atmospheres pressure, the diethyl sulphate yield had increased to 62 per cent and the ethylsulphuric acid yield diminished to 30 per cent of the sulphuric acid. In general, however, when the absorption is conducted at atmospheric pressure, using 96 per cent sulphuric acid, very little diethyl sulphate is formed, the main product being ethylsulphuric acid.

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[3] *Ber.*, 1903, **36**, 1988.

[4] *Bull. acad. roy. Belg.*, 1906, 7; *Chem. Soc. Abs.*, 1906, **90** (1), 476.

[5] *Ber.*, 1911, **44**, 1000.

[6] *Ann. chim. phys.*, 1895, (7) **4**, 101.

[7] *J.S.C.I.*, 1921, **40**, 14T.

[8] *Compt. rend.*, 1922, **175**, 585; *Chem. Abs.*, 1923, **17**, 259; *Bull. soc. chim.*, 1923, (4) **33**, 71; *Chem. Abs.*, 1923, **17**, 1208.

[9] *Atti Congr. Naz. Chim. Ind.*, 1924, 269; *Chem. Abs.*, 1925, **19**, 1402.

A detailed account of the various factors influencing the direct combination of ethylene with sulphuric acid is unnecessary at this stage since it is discussed at length in Chapter 13. It is of interest to note, however, that certain derivatives of sulphuric acid combine with ethylene to yield ethyl esters, as for example benzenesulphonic acid. Chlorosulphonic acid, when mixed with an equal weight of sulphuric acid (100%), was shown by Traube and Justh[10] to absorb ethylene rapidly and quantitatively from coke-oven gas with the production of ethyl chlorosulphonate, ($ClSO_3C_2H_5$, b.p. 155° to 160° C. at 760 mm.), which on hydrolysis yielded a mixture of ethyl alcohol, ethyl chloride, and sulphuric and hydrochloric acids.

The absorption of ethylene by means of ortho-, pyro-, and metaphosphoric acids at 140° C. and 1 atmosphere pressure was investigated by Müller,[11] who reported that ethyl dihydrogenphosphate was formed with orthophosphoric acid, and possibly also with the pyrophosphoric acid. The rate of absorption decreased as the quantity of dissolved gas increased. However, at the end of 17 days, 100 grams of orthophosphoric acid had absorbed 1200 cc. of ethylene at 115° to 145° C. The presence of a small amount of cuprous oxide or silver sulphate greatly increased the absorptive power of the acids.

The direct combination of ethylene with gaseous hydrogen chloride was first attempted by Berthelot[12] but without success, although this investigator was able to effect the combination of ethylene with hydrobromic and hydriodic acids with the production of the corresponding ethyl halides. Berl and Bitter[13] later found that the direct union of ethylene with hydrogen chloride would proceed in the presence of aluminum chloride as catalyst at temperatures of 100° C. and above (most advantageously at 130° to 170° C.) without the formation of appreciable quantities of by-products. Owing to the slowness of the reaction, prolonged contact with the catalyst was necessary for good yields of ethyl chloride. Much information regarding this reaction has been furnished by the work of Wibaut and his collaborators,[14] who carried out a systematic examination of the effects of various catalysts on this reaction under atmospheric pressure and at various temperatures. Bismuth trichloride on asbestos was reported to be the best catalyst for this reaction, other catalysts of lower activity being ferric chloride, vanadium trichloride and aluminum chloride. At ordinary temperatures in the presence of the bismuth trichloride the reaction proceeds slowly, but at higher temperatures (e.g., 200° to 215° C.) the yield of ethyl chloride is 80 per cent, or more, of the ethylene used. With the same catalyst, good yields of ethyl chloride could be obtained from mixtures of ethylene and coal gas or water gas, even at ethylene concentrations as low as one or two per cent.

A point of interest in regard to the combination of ethylene with hydrogen chloride is the fact that the reaction is a reversible one since ethyl chloride can be made to yield ethylene and hydrogen chloride when passed over heated catalysts. Many other reactions of a similar type, for example, the combination of ethylene, propylene, and higher olefins with anhydrous halogen acids, are also reversible under certain conditions. In the case of the combination of ethylene with hydrogen chloride according to the reaction

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[10] *Brennstoff-Chem.*, 1923, **4**, 150; *Chem. Abs.*, 1923, **17**, 3858.

[11] *Ber.*, 1925, **58B**, 2105.

[12] *Compt. rend.*, 1857, **44**, 1350; *ibid.*, 1860, **50**, 612.

[13] *Ber.*, 1924, **57B**, 95.

[14] Wibaut, Diekmann and Rutgers, *Proc. Acad. Sci. Amsterdam*, 1924, **27**, 671; *Chem. Abs.*, 1925, **19**, 1804; *Rec. trav. chim.*, 1928, **47**, 477; *Chem. Abs.*, 1928, **22**, 1949; *Z. Elektrochem.*, 1929, **35**, 602; *Chem. Abs.*, 1930, **24**, 1076.

$$C_2H_4 + HCl \rightleftharpoons C_2H_5Cl$$

the equilibrium is well over to the side of the ethyl chloride even at 200° C. but the amount of dissociation increases with rise in temperature. From a measurement of the equilibrium constants of this reaction at 114° and 124° C., which were found to be $K_{114} = 0.818 \times 10^{-8}$ and $K_{124} = 2.186 \times 10^{-8}$ where

$$K = \frac{p_{C_2H_4} \times p_{HCl}}{p_{C_2H_5Cl}}$$

Wibaut and Tidman have arrived at the value of 29.9 Cals. for the heat of reaction at constant pressure, which is in good agreement with Berthelot's thermal data.

The synthesis of ethyl chloride by the direct combination of ethylene with hydrogen chloride has attracted much attention probably largely from the point of view of the possible production of ethyl alcohol by the hydrolysis of the ethyl chloride formed. A number of interesting methods have been devised for carrying out such reactions. Thus, for example, Wibaut [15] prepared alkyl halides by passing a mixture of olefin and hydrogen chloride or bromide over a metal of the fifth group (e.g., a bismuth trihalide) at temperatures above 100° C. but not exceeding 250° C., the product being collected by absorption in activated charcoal. Higher temperatures are required when the olefin is diluted with other gases or air.

Suida [16] effected the combination of ethylene and hydrogen chloride, at atmospheric or increased pressure, in the presence of porous material impregnated with the liquid double compound of aluminum chloride and ethylene, $(C_4H_8AlCl_3)_x$, obtained by the passage of ethyl chloride over powdered aluminum chloride at 100° to 120° C. until it is completely converted into a dark brown liquid. On conducting a mixture of hydrogen chloride and ethylene over this catalyst at 90° C., a yield of 66 per cent is obtained. Suida [17] also described the direct combination of ethylene with hydrogen chloride at a pressure of 30 atmospheres and at temperatures below 50° C., conveniently at 10° C., in the presence of ferric chloride, aluminum chloride, or the molecular compounds of these with ethylene. As a modification of the above process, ethylene is combined with hydrogen chloride under 60 atmospheres pressure in the presence of an inert solvent, e.g., ethyl chloride itself, using aluminum chloride or its double compound with ethylene as a catalyst.[18] A similar combination of conditions has been suggested by Suida,[19] and the use of aluminum chloride to catalyze the combination of ethylene with hydrogen chloride has also been proposed by Webb.[20]

Acid-resistant adsorbents are recommended by Strange and Kane [21] as catalysts for the direct combination of low molecular weight olefins with hydrochloric or hydrobromic acid. The adsorbents mentioned are active carbon or activated charcoal, colloidal silica, or natural siliceous materials which have been dehydrated or extracted with acids, such as kieselguhr. The reaction takes place at temperatures below 120° C.

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[15] British Patent 209,722, 1923; *J.S.C.I.*, 1924, **43**, 731B; U. S. Patent 1,591,151, July 6, 1926; *Brit. Chem. Abs.* **B**, 1926, 721.

[16] German Patent 420,441, 1924; assigned to Chemische Fabrik vorm. Weiler-ter-Meer; *Brit. Chem. Abs.* **B**, 1926, 463.

[17] British Patent 229,298, 1925; *J.S.C.I.*, 1925, **44**, 653B. Also German Patent 417,170, 1924; *Brit. Chem. Abs.* **B**, 1926, 108.

[18] Chemische Fabrik vorm. Weiler-ter-Meer, British Patent 235,521, 1924; *J.S.C.I.*, 1925, **44**, 737B.

[19] German Patents 478,082, 1924; *Chem. Abs.*, 1929, **23**, 4231; and 485,434, 1924; *Chem. Abs.*, 1930, **24**, 866. Both patents assigned to I. G. Farbenindustrie A.-G.

[20] U. S. Patent 1,560,625, Nov. 10, 1925; assigned to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1926, 77.

[21] British Patent 353,032, 1930; *Brit. Chem. Abs.* **B**, 1931, 1085. Also French Patent 709,829, 1931; *Chem. Abs.*, 1932, **26**, 997.

The direct combination of ethylene with hydrogen bromide apparently occurs much more readily than in the case of hydrogen chloride. Thus, Berthelot,[22] on heating ethylene with a saturated solution of hydrobromic acid at 100° C. in a sealed tube for 100 hours, obtained a large quantity of ethyl bromide. Ethylene and a solution of hydriodic acid were found to react somewhat more rapidly. Gustavson [23] observed that the direct combination of ethylene with gaseous hydrogen bromide took place in the presence of aluminum bromide at 0° C. with the production of ethyl bromide and also other products. At higher temperatures, however, the reaction product was a complex mixture in which hydrocarbons and complex double compounds of aluminum bromide were present. Wibaut, Diekmann and Rutgers [24] observed that an efficient catalyst for this reaction was bismuth tribromide dispersed on asbestos. These workers noted that, in the presence of bismuth tribromide, the addition of hydrogen bromide to ethylene proceeds even at 20° C., and at atmospheric pressure at a much greater rate than that of hydrogen chloride under similar circumstances.

A method, which apparently combines dehydration of the alcohol to the olefins and subsequent addition of the halogen hydride, was described by Carlisle.[25] This consists in passing the vapors of the alcohol together with the halogen hydride over an aluminum oxide catalyst maintained at a temperature of 150° to 300° C.

Maass, Wright, and Sivertz [26] observed that in a mixture of liquid ethylene and liquid hydrogen bromide (under pressure) no reaction occurs at 0° C., although a slow reaction proceeded in the case of a mixture of liquid propylene and liquid hydrogen bromide at —78° C. Later Swann, Snow and Keyes [27] showed that ethylene heated under fairly high pressure (about 800 pounds per square inch) to 150° C. with moderately concentrated aqueous solutions of halogen acids (hydrobromic and hydriodic acids) yielded considerable quantities of ethyl halides together with very small amounts of free alcohol. Thus on heating 150 cc. of 45 per cent hydriodic acid together with ethylene, under an ethylene pressure of 800 pounds per square inch, for 3 hours at 150° C., 24 grams of the ethyl halide were obtained.

The direct esterification of ethylene by means of organic acids is apparently very difficult to effect. In the presence of condensing agents, such as sulphuric acid, esterification does take place. For example, Traube and Justh [28] found that ethylene and chlorosulphonic reacted in the presence of sulphuric acid to form ethyl chlorosulphonate. Ellis [29] proposed to esterify olefins with organic acids by heating in the presence of sulphuric or phosphoric acids. The olefins may be used directly, or dissolved in an inert solvent, such as a petroleum distillate. Or the olefins may be first absorbed in sulphuric acid and then the salt of an organic acid added, such as calcium acetate.[30]

In producing esters by the reaction between calcium acetate and alkyl sulphates in the presence of an inert organic solvent, the addition of a hygroscopic solid material, such as plaster of Paris or sodium sulphate, facilitates the separation of the calcium sulphate from the reaction mixture.[31]

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[22] *Compt. rend.*, 1850, 44, 1350; 1860, 50, 612.
[23] *J. prakt. Chem.*, 1886, (2) 34, 161; *Chem. Soc. Abs.*, 1886, 50, 999.
[24] *Rec. trav. chim.*, 1928, 47, 477; *Chem. Abs.*, 1928, 22, 1949.
[25] U. S. Patent 1,834,089, Dec. 1, 1931; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1933, 26, 997.
[26] *J.A.C.S.*, 1924, 46, 2664; 1925, 47, 2883.
[27] *Ind. Eng. Chem.*, 1930, 22, 1048.
[28] *Loc. cit.*
[29] U. S. Patent 1,365,052, Jan. 11, 1921; *Chem. Abs.*, 1921, 15, 865.
[30] Ellis *et al.*, U. S. Patents 1,365,050 and 1,365,051, Jan. 11, 1921; *Chem. Abs.*, 1921, 15, 865.

Alkyl esters may be obtained also by the action of an aqueous solution of hydrogen chloride (or bromide) on dialkyl sulphates or alkylsulphuric acids at temperatures above 100° C.[32] An alternate method consists in absorbing the olefin in sulphuric acid and causing the alkylsulphuric acid to react (by heating) with a carboxylic acid, e.g., acetic or benzoic acid. The addition of neutral sulphate or phosphate in quantity sufficient to bind the free sulphuric acid present and that formed during the reaction is necessary.[33]

PROPYLENE

Propylene is capable of combining with both mineral and organic acids much more readily than ethylene. Indeed it appears to be a general rule that the chemical reactivity of the olefin hydrocarbons increases with increasing molecular weight up to a certain maximum and then declines.

In comparing the additive powers of ethylene, propylene, n- and iso-butylene, trimethyl- and tetramethylethylene, and also di-isobutylene with various mineral acids, Brunel and Probeck[34] found that a maximum was obtained with isobutylene.

Although, as stated, the union of propylene with sulphuric acid takes place much more readily than in the case of ethylene, isopropylsulphuric acid, though formed in quantity under certain circumstances, is by no means the only product of the reaction. A number of side reactions take place and in order to obtain appreciable quantities of isopropyl alcohol it is necessary to adjust the conditions very carefully. Ellis[35] has shown that for the production of isopropyl alcohol the olefin should be dissolved in 87 per cent acid (d 1.8). Absorption can be continued until the density has fallen to 1.4, and during absorption the temperature of the acid should be maintained at 20° to 40° C. The gases may be absorbed directly by the acid, or in the presence of a diluent such as a petroleum distillate.

Any substance which is miscible with the olefins and unreactive with the acid is a satisfactory diluent. The mechanism by which this diluent prevents polymerization is probably as follows:

(1) The diluent molecules are right beside the reacting olefin molecules at the interface and therefore absorb the heat of reaction at the point where it is evolved, and thus lessen local overheating.

(2) If pure olefins react with acid, the instant some olefin molecules are absorbed by the acid absolutely fresh olefin molecules rush to the interface and there are capable of instant reaction with the further evolution of heat. When, however, a diluent is present, then, after the first instant of reaction during which only the surface layer of reactive olefin molecules in the hydrocarbon mixture react, the acid is left in contact with an insulating layer of inert hydrocarbon. The reaction therefore ceases, except as fresh reactive olefin molecules diffuse up to the acid surface through this insulating layer of hydrocarbons. These diffusion processes are notably slow, and the reaction rate is therefore retarded. This gives time for the heat evolved at the interface to dissipate itself and local overheating is again eliminated.

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[31] Archibald and Lebo, U. S. Patent 1,844,536, Feb. 9, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1932, **26**, 1945.

[32] I. G. Farbenindustrie A.-G., British Patent 370,211, 1930; *Chem. Abs.*, 1933, **27**, 2965. For the preparation of acetates by a simpler procedure, see I. G. Farbenindustrie A.-G., U. S. Patent 1,910,818, May 23, 1933; *Chem. Abs.*, 1933, **27**, 3952; British Patent 364,701, 1930; *Chem. Abs.*, 1933, **27**, 1642; German Patent 574,833, 1933; *Chem. Abs.*, 1933, **27**, 4543; Merley, U. S. Patent 1,898,737, Feb. 21, 1933; assigned to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 2692.

[33] Lommel and Engelhardt, U. S. Patent 1,903,868, Apr. 18, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3223.

[34] *Amer. Chem. J.*, 1910, **44**, 437.

[35] Ellis *et al.*, U. S. Patents 1,464,153, Aug. 7, 1923; 1,486,646, Mar. 11, 1924; 1,486,647, Mar. 11, 1924.

> (3) As far as the olefinic constituent of the mixture is concerned sulphation is a unimolecular reaction, and proportional to the olefin concentration at the interface. Polymerization, on the other hand, must from its very nature be proportional to the square of the olefin concentration at the interface, or perhaps even a higher power. Furthermore, it is the interfacial concentration alone that counts in this respect. Therefore dilution tremendously reduces the ratio of polymerization to sulphation and makes it possible to raise the temperature and thus avoid the cost of low-temperature refrigeration. At the same time, increasing the sulphation rate by increasing the temperature far more than compensates for the reduction in sulphation rate due to dilution. Thus the reaction is made commercially possible.

Liquid hydrocarbon diluents are employed by Ellis and by Mann and Williams.[36] If an easily volatile diluent starts to heat at the interface, vapor will be formed, and since vapor formation absorbs a large quantity of heat the interface will therefore be cooled. Furthermore, the vapor insulates the hydrocarbon liquid from the acid, thereby slowing the reaction and hence also the evolution of heat. This is also an important auxiliary factor in making the conditions of sulphation commercially effective.

After absorption is completed the acid layer is diluted with water, to bring about hydrolysis, and then distilled. Isopropyl alcohol is obtained in the distillate.

In their work Plant and Sidgwick[37] observed that, after acid of 97 per cent strength had absorbed 50 per cent by weight of propylene in 2 hours, a colorless oil separated. This oil, boiling from 55° to 155° C. at 30 mm., was considered by them to be a mixture of open-chain secondary alcohols, produced by the action of sulphuric acid on propylene polymers. Ormandy and Craven[38] later reported, however, that the oily products obtained by the action of 98 per cent sulphuric acid on propylene consist partly of paraffin hydrocarbons. Undoubtedly the action of sulphuric acid on propylene and the higher olefins, under certain circumstances, may lead to a complex mixture of products. Under other conditions, good yields of isopropylsulphuric acid, and then isopropyl alcohol, may be obtained.

The reaction of propylene with halogen acids has been studied by Maass, Wright and Sivertz,[39] who found that in a mixture of liquid propylene and liquid hydrogen bromide at —78° C. a slow reaction occurs resulting in the formation of isopropyl bromide and in addition another product of higher boiling point, probably a hexyl bromide. Liquid hydrogen chloride and liquid propylene reacted slowly at 20° C. forming besides isopropyl chloride an appreciable amount of a higher boiling substance, later[40] identified as a hexyl chloride (probably 2-chloro-4-methylpentane). The velocity of the reaction between propylene and hydrogen chloride in the liquid state increased with rise in temperature; above the critical temperature, however, the reaction velocity became almost zero.[41] It was found, moreover, that in a gaseous mixture of hydrogen chloride and propylene enclosed in a glass vessel (without catalysts) no reaction occurred at room temperature even when the experiment was continued for 400 days. Some work on the addition of propylene to gaseous hydrogen chloride and bromide has been carried out by Wibaut and his collaborators,[42] who have shown that in the presence of a bismuth chloride-asbestos catalyst hydrogen chloride reacts vigorously with propylene at room temperature, the product being 2-chloropropane (isopropyl chloride). At 80° to 90° C., in the presence of this catalyst, the yield of isopropyl chloride was 91 per cent based on the propylene used. Gaseous hydrogen bromide was found to react with propylene at 20° C. in the presence of pure asbestos, though bismuth tribromide dispersed on glass wool was the best catalyst. In the presence of the latter material, the combination of hydrogen bromide and propylene occurred readily at 20° C. (the temperature rising to 40° C. spontaneously) and the yield of 2-bromopropane was 93 per cent of the theoretical. Antimony tribromide also was observed to exert considerable catalytic influence on the reaction. Furthermore, after the methyl group in propylene is halogenated, the addition of a halogen acid yields 1,3-dihalogen propane, a reagent used in organic syntheses.

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[36] U. S. Patent 1,365,043, Jan. 11, 1921; *J.S.C.I.*, 1921, **40**, 162A.
[37] *J.S.C.I.*, 1921, **40**, 17T.
[38] *J.S.C.I.*, 1928, **47**, 317T.
[39] *J.A.C.S.*, 1924, **46**, 2664; 1925, **47**, 2883.
[40] Sutherland and Maass, *Trans. Roy. Soc. Canada*, 1926, **20**, 499; *Chem. Abs.*, 1927, **21**, 2657.
[41] Sutherland and Maass, *Canadian J. Research*, 1931, **5**, 48; *Brit. Chem. Abs.* **A**, 1931, 1239.
[42] *Loc. cit.*

The conversion of propylene into isopropyl chloride by direct combination with hydrogen chloride according to the reaction:

$$C_3H_6 + HCl \rightleftharpoons C_3H_7Cl$$

has been the basis for a number of processes, particularly those of Wibaut,[43] Curme,[44] and the T. Goldschmidt A.-G.[45] Curme proposed to make isopropyl chloride by allowing anhydrous propylene to react with hydrogen chloride under 15 atmospheres pressure, a solvent being added if desired. In the process of the T. Goldschmidt A.-G. propylene and its higher homologues may be converted into the corresponding alkyl chlorides preferentially, so that any admixed ethylene is not attacked, by passing these olefins together with hydrogen chloride over a contact mass of anhydrous iron chloride at ordinary temperatures.

Although the reaction between propylene and hydrogen bromide is generally assumed to give isopropyl bromide, nevertheless, the addition of modifying agents to the reacting substances makes it possible to obtain either n- or isopropyl bromide as the main product. In the presence of air or antioxidants (e.g., diphenylamine) isopropyl bromide is obtained almost exclusively, though the presence of peroxides (e.g., benzoyl peroxide), gives practically quantitative yields of n-propyl bromide.[46]

Not a great deal of work has been done on the direct combination of propylene with organic acids, although this reaction is capable of being achieved under certain conditions with the production of esters of isopropyl alcohol. Thus, Ellis [47] has proposed the esterification of olefins by organic acids in the presence of sulphuric acid, or by absorbing them in sulphuric acid and then adding the salt of an organic acid. The production of ethyl acetate was accomplished by Oehme [48] by treating a solution of ethylene in concentrated sulphuric acid with glacial acetic acid. Also, Woolcock [49] reported that good yields of isopropyl acetate may be obtained by absorbing propylene in a mixture of glacial acetic and concentrated sulphuric acids. On treating a mixture of equal volumes of 99.5 per cent sulphuric acid and glacial acetic acid with gaseous propylene at 40° C. and at atmospheric pressure until no more propylene was absorbed, the yield of isopropyl acetate was 27 per cent of the propylene absorbed while 53 per cent was recovered as isopropyl alcohol (through the intermediate formation of isopropylsulphuric acid), representing a total yield of 80 per cent, based on the amount of propylene absorbed.

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[43] U. S. Patent 1,591,151, July 6, 1926; *Brit. Chem. Abs.* **B**, 1926, 721.

[44] U. S. Patent 1,545,742, July 14, 1925; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1925, **19**, 2830.

[45] British Patent 235,547. 1925; *J.S.C.I.*, 1925, **44**, 738B.

[46] Kharasch, McNab and Mayo, *J.A.C.S.*, 1933, **55**, 2531.

[47] *Loc. cit.*; U. S. Patents 1,365,050 and 1,365,052, Jan. 11, 1921; *J.S.C.I.*, 1921, **40**, 162A.

[48] German Patent 372,717, 1919; assigned to Chem. Fabrik Kalk G.m.b.H.; *J.S.C.I.*, 1923, **42**, 1200A.

[49] British Patent 334,228, 1930; assigned to Imperial Chemicals Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 1058.

Suida[50] recommended that the addition of organic acids to olefins, in the presence of sulphuric acid as a catalyst, be effected at 180° C. and under pressure of 20 to 50 atmospheres.

Direct combination of olefins and aliphatic carboxylic acids takes place in the presence of the chlorides, bromides, phosphates or sulphates of heavy metals, as well as sulphuric or phosphoric acid or their acid salts.[51] The reaction is carried out at any desired pressure and at a temperature above the boiling point of the ester (at the pressure employed), thus allowing its removal from the reaction zone as a vapor.

BUTENES

The tendency of the olefin hydrocarbons having four or more carbon atoms per molecule to combine with acids with the formation of the esters of the corresponding secondary and tertiary alcohols is relatively great in comparison with ethylene and propylene. Of the three isomeric butylenes, isobutylene is much more reactive toward acids and forms the esters of tertiary butanol with considerable ease. The other two butylenes both give rise to esters of the secondary alcohol, namely $CH_3CH_2CHOHCH_3$.

The reaction of the three butylenes with sulphuric acid to yield alkylsulphuric esters, and then, by hydrolysis, the corresponding alcohols, is now well known. Much less concentrated acid may be used to effect the reaction than with ethylene and propylene. The use of too concentrated acid results in the formation of undesirable by-products. This reaction will be discussed in detail in Chapter 16, which describes the production of the higher aliphatic alcohols.

The reaction between hydrogen chloride and the three butylenes has been investigated by Coffin, Sutherland and Maass.[52] The rates of reaction with anhydrous liquid hydrogen chloride were shown to differ so greatly that it is possible to utilize this reaction as a means of separating the isomers. Thus, isobutylene is completely converted into tertiary butyl chloride by hydrogen chloride gas at —78° C., while the other two butylenes are scarcely affected. Of the chlorides produced, only the secondary is formed from 1- and 2-butene, while isobutylene yields only the tertiary chloride. In the reaction between 1-butene and 2-butene and hydrogen chloride, a secondary product was also formed which was shown to be an octyl chloride, readily decomposable into octylene and hydrogen chloride. The remarkable activity of isobutylene in combining with halogen acids has been known for many years. Zalessky[53] found that on heating the hydrocarbon with concentrated hydrochloric acid to 100° C. it was converted into tertiary butyl chloride and Favorsky[54] noted that the reaction between hydrogen chloride and isobutylene occurred at 100° C. in the presence of asbestos. The observation of Scheschukoff[55] that isobutylene reacts with aqueous hydriodic acid at 0° C. to yield tertiary butyl iodide was later somewhat elaborated by Michael and Brunel,[56] who found that mixtures of tertiary iodide and tertiary alcohol were simultaneously produced, the composition of the mixture being dependent upon the concentration of the hydriodic acid used. When 60 per cent hydriodic acid was used the product was the iodide almost exclusively but with acids of lower concentration increasing proportions of free tertiary alcohol were found to be present. Various proposals for the direct addition of hydrogen chloride to butylenes have been made, such as those of the T. Goldschmidt A.-G[57] and Blanchet.[58].

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[50] U. S. Patent 1,836,135, Dec. 15, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 994.

[51] Strange and Kane, British Patent 398,527, 1932; *Brit. Chem. Abs.* **B**, 1933, 954. See also Graves, U. S. Patent 1,915,308, June 27, 1933; assigned to E. I. duPont de Nemours and Co.; *Chem. Abs.*, 1933, 27, 4243.

[52] *Canadian J. Research*, 1930, 2, 267; *Chem. Abs.*, 1930, 24, 3750.

[53] *Ber.*, 1873, 5, 480.

[54] *Ann.*, 1907, 354, 334.

[55] *J. Russ. Phys. Chem. Soc.*, 1886, 18, 207; *Chem. Soc. Abs.*, 1886, 50, 680.

[56] *Amer. Chem. J.*, 1912, 48, 269.

The direct combination of butylene with acetic acid was described by the Bataafsche Petroleum Maatschappij.[59] Their method consists in heating a mixture of the olefin, glacial acetic and sulphuric acids, and ferro- or ferri-cyanides (as catalysts) in an autoclave. A 70 per cent yield of butyl acetate and also a small quantity of butyl alcohol is said to result. Frolich and Young[60] suggested passing olefins, particularly butylene, countercurrent to a stream of glacial acetic acid, containing some sulphuric acid, at temperatures of 50° C. or higher. Pressures of 100 to 180 pounds per square inch may be employed. The esters are extracted from the acid with a low-boiling solvent, e.g., pentane or hexane, and the solvent and esters separated by distillation.

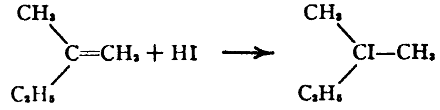
HIGHER OLEFINS

The ease of addition of sulphuric acid to some of the higher olefins is remarkable and the products are the alkylsulphuric esters corresponding to the secondary and tertiary alcohols. These are discussed later in connection with the synthesis of higher alcohols from olefins (Chapter 16).

Much of the earlier work on the direct combination of halogen acids with the higher olefins is of questionable value since the materials treated probably were mixtures of isomeric olefins. Nevertheless, sufficient information was collected to show that the pentenes and hexenes can combine with halogen acids with great ease to yield the corresponding alkyl halides. Wagner and Saytzeff[61] found that 2-pentene reacts readily with aqueous hydriodic acid to yield 3-iodopentane, a similar product being also obtained from 1-pentene. Isopropylethylene combines with hydriodic acid at room temperature to yield the corresponding secondary iodide,

$$(CH_3)_2CHCH{=}CH_2 + HI \longrightarrow (CH_3)_2CHCHICH_3$$

but this reaction does not take place at —20° C. at which temperature methylethylethylene readily combines with hydriodic acid to yield tertiary amyl iodide,



$$\begin{matrix} CH_3 \\ \quad\diagdown \\ \quad\; C{=}CH_2 \\ \quad\diagup \\ C_2H_5 \end{matrix} + HI \longrightarrow \begin{matrix} CH_3 \\ \quad\diagdown \\ \quad\; CI{-}CH_3 \\ \quad\diagup \\ C_2H_5 \end{matrix}$$

Isopropylethylene or methylethylethylene does not react with hydrogen chloride at —80° C. in the absence of a catalyst.[62] However, when aluminum chloride is present, isopropylethylene reacts to yield mostly 2-methyl-3-chloro-butane. The main product from methylethylethylene is 2-chloro-2-methylbutane.

A critical study of the addition of hydrogen bromide to 2-pentene was made by Lucas and Moyse.[63] The pure pentene was distilled between 35° and 37° C.

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[57] British Patent 235,547, 1925; *J.S.C.I.*, 1925, 738B.

[58] British Patent 251,652, 1926; assigned to Soc. Anon. d'Explosifs et de Prod. Chim.; *Brit. Chem. Abs.* B, 1927, 836.

[59] British Patent 323,748, 1928; *Brit. Chem. Abs.* B, 1930, 359.

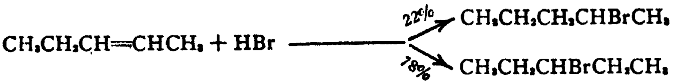
[60] U. S. Patent 1,877,291, Sept. 13, 1932; *Chem. Abs.*, 1933, 27, 101; British Patent 362,215, 1931; *Chem. Abs.*, 1933, 27, 996; both patents assigned to Standard Oil Development Co.

[61] *Ann.*, 1876, 179, 313; Wischnegradsky, *Ann.*, 1878, 190, 356; *Chem. Soc. Abs.*, 1878, 34, 393; Brochet, *Bull. soc. chim.*, 1892, (3) 7, 567.

[62] Leendertse, Tulleners, Waterman, *Rec. trav. chim.*, 1933, 52, 515; *Chem. Abs.*, 1933, 27, 5051.

[63] *J.A.C.S.*, 1925, 47, 1459.

through a Hempel column into a cold solution of 43 grams of hydrogen bromide in 60 grams of glacial acetic acid. The resulting product consisted of a mixture of 78 per cent of 3-bromopentane and 22 per cent of 2-bromopentane (this



$$\begin{tikzcd}[column sep=small] & CH_3CH_2CH_2CHBrCH_3 \\ CH_3CH_2CH{=}CHCH_3 + HBr \arrow[ur, "22\%"] \arrow[dr, "78\%"'] & \\ & CH_3CH_2CHBrCH_2CH_3 \end{tikzcd}$$

result being considered in agreement with the prediction made on the basis of the theory of electron displacement). An extended study of orientation in the addition of halogens and hydrogen halides to simple ethylene derivatives has also been made by Ingold and his collaborators.[63a]

Some interesting results have been reported by Piotrowski and Winkler[64] on the addition of hydrogen chloride to unsaturated hydrocarbons. The hydrocarbon mixture used in their experiments was a fraction of cracked gasoline (boiling range of 20° to 40° C.) and contained about 31 per cent by weight of amylenes. The hydrocarbon vapors together with a slight excess of hydrogen chloride were passed over heated catalysts supported on activated charcoal and held in two tubes. When the temperature of the first tube was maintained at 75° C. and that of the second tube at 150° C. the products of the reaction were predominantly secondary chlorides. If the sequence of these temperatures was reversed, then a mixture of all possible chlorides was obtained. The presence of moisture interfered with the formation of the secondary chlorides, while its absence caused no detrimental effects. The catalysts were poisoned by sulphur compounds, and the latter should therefore be removed.

The catalysts employed were the chlorides of bivalent, tervalent, and quadrivalent metals, and could be divided into three groups: (1) ferric and chromic chlorides which were inactive; (2) the chlorides of mercury, copper, cadmium, manganese, bismuth, aluminum and antimony which were only slightly active; and (3) zinc and stannic chlorides which were active, the latter[65] giving a practically quantitative yield of the monochlorides of amylene.

It is said that amylene and acetic acid react at ordinary temperatures in the presence of zinc chloride.[66] The yield of acetates is low, however, because of the formation of polymers. Nernst and Hohmann[67] have shown that, when heated in sealed tubes at 100° C., amylene will combine with di- and tri-chloracetic, tri-chlorolactic, salicylic and benzoic acids. With trichloracetic acid a maximum yield of 88 per cent of the trichloracetic amyl ester was obtained.

The preparation of amyl acetate by the direct esterification of amylene is described by Brooks.[68] Sucharda and Mazonski[69] state that amylene and hexene, occurring in low-boiling cracked petroleum distillates, can be converted almost quantitatively into the corresponding secondary and tertiary formates by formic acid in the presence of sulphuric acid.

The combination of the higher open-chain olefins with organic acid takes place much more readily than with the lower homologues. Béhal and Desgrez[70] brought about this direct combination by heating the reactants together in sealed tubes. Thus, on heating caprylene with three volumes of glacial acetic acid for 24 hours at 300° C. a good yield of octyl acetate was obtained. Under similar conditions heptylene yielded a secondary heptyl acetate, while on heating allyl acetate with glacial acetic acid, at 275° to 285° C., there was produced the diacetate of propylene glycol,

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[63a] Ingold and Smith (*J.C.S.*, 1931, 2742) studied additions with iodine monochloride and Ingold and Ramsden (*J.C.S.*, 1931, 2746), the additions of hydrogen halides to propylene and 1-pentene. The mechanism of the additions of halogens and hydrogen halides has been discussed by Ingold and Smith (*J.C.S.*, 1931, 2752).

[64] *Przemysl Chem.*, 1931, 15, 25; *Chem. Abs.*, 1931, 25, 1794. Also, *J. Inst. Pet. Tech.*, 1931, 17, 225.

[65] Piotrowski and Winkler; German Patent 574,802, 1933; assigned to Galicyjskie Towarzystwo Naftowe "Galicja" Sp. Akc.; *Chem. Abs.*, 1933, 27, 4543.

[66] Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, 1922, 125.

[67] *Z. phys. Chem.*, 1893, 11, 352; *Chem. Soc. Abs.*, 1893, 64 (1), 449.

[68] U. S. Patent 1,894,662, Jan. 17, 1933; assigned to Petroleum Chemical Corp.; *Chem. Abs.*, 1933, 27, 2459.

[69] *Przemysl Chem.*, 1933, 17, 41; *Brit. Chem. Abs.* B, 1933, 497.

$$CH_3CH(OOCCH_3)CH_2(OOCCH_3).$$

In the direct hydration of various olefins under the influence of aqueous oxalic acid solutions as observed by Miklaschewsky,[71] the oxalic acid ester is probably an intermediate product. The direct combination of olefins with organic acids is facilitated by the addition of dehydrating agents such as zinc chloride or sulphuric acid to the mixture. Thus, on allowing equimolecular quantities of hydrocarbon and organic acid to stand at 20° C. for 24 hours in the presence of anhydrous zinc chloride (12 to 20 grams of zinc chloride per 100 grams of hydrocarbon), Kondakow[72] found that considerable combination took place, the yield of ester being 20 per cent or more. In this way trimethylethylene yields the acetate of dimethylethylcarbinol. Bertram and Walbaum[73] used a mixture of glacial acetic acid and 50 per cent sulphuric acid. This method is especially applicable to the terpene series, e.g., the conversion of camphene into isobornyl acetate and of pinene into bornyl esters.

Many cyclic olefins of the terpene class are known to react very readily in glacial acetic acid or ether solution. Thus, for example, sylvestrene[74] with two double bonds in its molecule combines with hydrogen chloride to yield a crystalline dihydrochloride, and carvestrene[75] similarly combines with two molecules of hydrogen bromide in glacial acetic acid solution to yield a dihydrobromide thus: $C_{10}H_{16} + 2HBr \rightarrow C_{10}H_{18}Br_2$, two double bonds being saturated in the process. The addition of halogen acids to pinene and other terpene hydrocarbons is well known.

The fact that the unsaturated cyclic hydrocarbon pinene (present in turpentine) can combine directly with acids[76] to yield bornyl esters has provided a commercial method for the synthesis of camphor. The esterification of pinene can also be effected by organic acids. Thus, bornyl trichloroacetate is readily prepared by heating pinene with trichloroacetic acid,[77] and bornyl oxalate by heating pinene with anhydrous oxalic acid at 100° C. The bornyl acetate can be hydrolyzed by lime and the borneol obtained can then be oxidized to yield camphor.[78] Esters of borneol and isoborneol are made by the reaction of formic or acetic acid with camphene in the presence of boron fluoride.[79] According to Schwyzer[80] the technical esterification of pinene is now carried out by means of oxalic acid or, better, by salicylic acid, the use of the latter resulting in the production of less by-products. The bornyl esters are then hydrolyzed to borneol which is oxidized to camphor.

[70] *Compt. rend.*, 1892, 114, 676; *Chem. Soc. Abs.*, 1892, **62**, 1162.

[71] *Ber.*, 1891, **24**, Ref. 269.

[72] *J. prakt. Chem.*, 1893, (2) **48**, 479; *Chem. Soc. Abs.*, 1894, **66**, 113.

[73] *J. prakt. Chem.*, 1894, (2) **49**, 1; *Chem. Soc. Abs.*, 1894, **66**, 204.

[74] Wallach, *Ann.*, 1887, **239**, 1; *Chem. Abs.*, 1887, **52**, 965.

[75] Baeyer, *Ber.*, 1894, **27**, 3488.

[76] Bouchardat and Lafont, *Compt. rend.*, 1891, **113**, 551; *Chem. Soc. Abs.*, 1892, **62**, 199; *Compt. rend.*, 1894, **118**, 248; *Chem. Soc. Abs.*, 1894, **66** (1), 255; *Compt. rend.*, 1897, **125**, 111; *Chem. Soc. Abs.*, 1897, **74** (1), 442.

[77] Reychler, *Ber.*, 1896, **29**, 696. Wagner and Brickner, *Ber.*, 1899, **32**, 2306.

[78] Ampere Electro-Chem. Co., German Patent 134,553, 1902; *Chem. Zentr.*, 1902, **2**, 975.

[79] Hilcken, U. S. Patent 1,902,364, Mar. 21, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3223.

[80] *Pharm. Zeit.*, 1930, **75**, 1275; *Chem. Abs.*, 1931, **25**, 508.

Chapter 13

Production of Ethyl Alcohol from Ethylene

The production of most of the primary alcohols is carried out by fermentation processes, by destructive distillation of carbonaceous material, or by the saponification of certain natural esters. From petroleum hydrocarbons as raw materials only the first two primary alcohols are produced on a large scale, namely methyl alcohol or methanol and ethyl alcohol or ethanol.

As shown in the preceding chapters the addition of the elements of water to olefins, either by direct hydration or indirectly by means of acids, results in the formation of alcohols. Ethylene is the sole olefin which under these conditions yields only a primary alcohol, ethyl alcohol; all the other olefins yield mixtures of primary and secondary, or secondary and tertiary alcohols.

Ethyl alcohol is a substance of immense industrial value as a solvent, as a chemical intermediate, and as a fuel for internal combustion engines. It still is very largely manufactured at the present time by the fermentation of various types of carbohydrate materials. It has long been known that ethyl alcohol could be prepared from ethylene in a number of ways but the industrial application of these reactions has until recently been prevented by economic considerations. The ethylene of coke-oven gas, amounting to only 3 per cent by volume of that gas, was the main source of that material until a decade ago. During the past few years large quantities of ethylene and other olefins have been produced in commercial cracking operations, a factor which has greatly stimulated interest in the various processes for the manufacture of alcohols from the lower olefins.

Two procedures are available for the conversion of ethylene into ethyl alcohol, namely:

(1) Direct hydration according to the reaction:

$$CH_2{=}CH_2 + H_2O \longrightarrow C_2H_5OH$$

This has been discussed in some detail (Chapter 11) and does not appear to be very promising, although continuing to be a subject of active investigation.

(2) Combination of ethylene with various acids, followed by hydrolysis of the resulting ethyl ester.

In this chapter the well-known sulphuric acid process will be discussed since this alone seems to have attained a measure of success. The reactions involved in the production of ethylsulphuric acid followed by hydrolysis of this substance may be represented by:

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5HSO_4$$
$$C_2H_5HSO_4 + H_2O \longrightarrow C_2H_5OH + H_2SO_4$$

The reaction between ethylene and sulphuric acid to yield ethylsulphuric acid was studied in Faraday's laboratory as early as 1827 by Hennell, who used gas containing olefins and suggested the production "of either ether or alcohol according to circumstances which are under perfect control".[1]

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[1] *Proc. Roy. Soc. (London)*, 1828, 118, 365.

Berthelot,[2] however, was the first to investigate the reaction from the point of view of the synthesis of alcohol from gases containing ethylene. He found that the absorption of ethylene by concentrated sulphuric acid was very slow at ordinary temperatures even with good agitation. More rapid absorption occurred at high temperatures though some loss of acid from oxidation and charring of the olefin also took place. In another publication Berthelot[3] described his experiments on the velocity of absorption of ethylene in sulphuric acid as well as the separation of olefins from illuminating gas by means of iodine. He was able to show that alcohol could be made by processes other than fermentation. The absorption of olefins by sulphuric acid and their subsequent conversion into ether was also discussed.[4]

Some interesting views were expressed by Payen,[5] who criticized the attempts being made at that time to produce alcohol from the olefins in illuminating gas.

> "A new process for the production of alcohol from illuminating gas is said to have been recently discovered whereby one hectoliter of alcohol can be made for 25 francs. As a matter of fact one liter of alcohol produced from oil-forming gas was shown at the London Industrial Exhibition; this oil-forming gas, however, was the result of decomposing alcohol according to usual laboratory methods, and as is well known the content of this same gas in illuminating gas does not exceed 10 per cent. The costs of making this liter of alcohol, which was exhibited in London, are said to have amounted to not less than 100 francs. . . . There is also a rumor that alcohol production is being carried out on a large scale at Saint Quentin, and that coal is fed into one side of the apparatus while alcohol is discharged on the other side. According to reliable information which I have received, only one or two liters of alcohol have been taxed up to the present and furthermore it has not yet been definitely proved that this alcohol was produced by the application of the new method.
>
> "Benjamin Corenwinder has shown in a letter to Pasteur that *a priori* this method of production would be very difficult and expensive, because one part of alcohol requires ten parts of sulphuric acid, and furthermore the purification of the alcohol is not an easy task. This purification, however, can be accomplished by means of olive oil, which after continued use imparts a very rancid odor to the alcohol.
>
> "I therefore do not believe the rumor mentioned above has any serious basis, and that alcohol production from oil-forming gas, while scientifically possible, has not yet been developed into a practical and economical process."

According to Goriainow and Butlerow,[6] ethylene is not dissolved by sulphuric acid at ordinary temperatures but at 100° C. (and still better between 160° and 175° C.) the gas is very rapidly absorbed. By subsequently diluting and distilling the acid liquor they obtained a considerable quantity of alcohol. Later work appears to indicate, however, that at the higher temperatures mentioned considerable charring and oxidation occur.

Fritzsche[7] was the first to attempt the large-scale manufacture of ethyl alcohol and diethyl ether from ethylene by the sulphuric acid process. The source of ethylene was initially coal gas stripped of its higher unsaturated hydrocarbon content by washing with 62° to 64° Bé sulphuric acid at ordinary temperature. Ethylene was absorbed from this purified gas in hot concentrated sulphuric acid at temperatures of 110° to 120° C., at which temperature the absorption is rapid and the decomposition of the resulting ethylsulphuric acid slight. According to Fritzsche, the resulting ethylsulphuric acid may be worked up at will into alcohol, ether or esters of organic acids. Alcohol or ether may be obtained by heating with water and esters by the addition of the salts of organic acids. The cost of reconcentrating the dilute acid was considered to be so great as to make it doubtful if alcohol could be produced commercially in this way.

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[2] *Compt. rend.*, 1855, 40, 10.
[3] *Ann. chim. phys.*, 1855, 43 (3), 385; *Ann.*, 1855, 94, 78.
[4] *Compt. rend.*, 1855, 40, 102.
[5] *Dinglers Polytech. J.*, 1863, 167, 236.
[6] *Ann. Chem. Phar.*, 1874, 169, 196; *Ber.*, 1873, 6, 196.
[7] *Chemische Industrie*, 1897, 20, 266; 1898, 21, 33.

The absorption of ethylene in sulphuric acid, followed by the addition of water, distilling the mixture, and determining the quantity of alcohol in the distillate is the basis of a method for the quantitative estimation of ethylene in gas mixtures.[8]

The production of diethyl ether from the mixture of sulphuric and ethylsulphuric acids obtained by absorbing ethylene in concentrated sulphuric acid was discussed by Fritzsche.[9] The method involves the use of four distilling vessels *A, B, C,* and *D,* connected in such a way that the vapors evolved from *A* pass through the liquids contained in *B, C,* and *D,* and are condensed beyond *D.* Each vessel is charged with the same volume of ethylsulphuric acid mixture, the liquid in *A* being diluted with 35 per cent of water, that in *B,* with 22 per cent, that in *C,* with 10 per cent, and that in *D* being undiluted. The contents of *A* are strongly heated and the liquid in *B* is only slightly warmed with the result that pure ether passes beyond *D* and is condensed. When the liquid in *A* is sufficiently concentrated it is run out, the liquid in *B* transferred to *A,* that in *C* to *B,* and that in *D* to *C;* after which *D* is charged with a further quantity of undiluted acid. The dilutions in the first three containers are adjusted as before and the distillation continued until *A* is again concentrated. Instead of removing the charge in *A* after each operation, the process can be made to work continuously by using an apparatus in which the concentrated acid passes in a constant stream into the vessel, water being introduced continuously into the apparatus to maintain the correct dilution.

Later Fritzsche[10] recorded some results obtained with his process in the United States where large quantities of oil gas, containing 22 per cent or more of ethylene, were available. The most important consideration was the removal of higher olefins and diolefins by a preliminary wash with 66° Bé sulphuric acid at temperatures below 40° C. Brooks[11] removed higher monolefins and diolefins from cracked oil gas by subjecting the mixture to pressures of 300 to 550 pounds per square inch. At these pressures a large amount of undesirable compounds condense out leaving a gas containing a substantially high ethylene fraction.

In the course of an investigation of the methods of analysis of gaseous unsaturated hydrocarbons, Lebeau and Damiens[12] observed that certain substances dissolved or suspended in concentrated sulphuric acid were capable of accelerating the absorption of ethylene to a marked degree. It was found, for example, that solutions of vanadic and uranic acids, as well as uranyl sulphate, in sulphuric acid were excellent catalysts, and that tungstic and molybdic acids possessed somewhat less catalytic power. These catalysts were only active after being reduced by mercury or some other metal in sulphuric acid solution, the reduction being frequently accompanied by marked color changes.

An attempt to manufacture alcohol by the sulphuric acid reaction was made by Bury and Ollander[13] and Tidman[14] at Skinningrove (England) about 1919 to 1921, using coke-oven gas containing about 2 per cent of ethylene as the raw material. The best strength of acid was found to be between 95 and 95.8 per cent and the optimum temperature range 60° to 80° C. The absorption was carried out in towers packed with fused silica but mechanical agitators were considered more suitable. The interesting observation was made that the addition of silica to the sulphuric acid increased the speed of absorption by 5 per cent. This was considered to be a catalytic reaction since, in a repetition of the experiment under similar conditions except that the silica was coated with a slime of lead sulphate, the absorption was not so rapid. The efficiency of absorption was about 70 per cent, and after saturation the acid was diluted to 64 per cent with water and distilled under a vacuum of 26.5 inches, the temperature rising from 94° to 146° C. during the distillation. This operation could be performed satisfactorily without frothing. The acid residue showed 80 per cent sulphuric acid and the distillate contained 15 per cent alcohol. Attempts to recover the alcohol from the absorption product by means of a countercurrent flow of acid and superheated steam failed because of the large amounts of froth produced. Concentrated alcohol produced in this way possessed an objectionable odor which was traced to the presence of certain impurities, notably diethylene disulphide, resulting from the action of ethylene on the hydrogen sulphide present in the gas. Commercial development was handicapped by the large amount of acid required, namely 6 to 7 pounds of acid per pound of ethylene, and the expensive reconcentration necessary.

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[8] Fritzsche, *Z. angew. Chem.*, 1896, 9, 456; *Chem. Soc. Abs.*, 1896, 70 (2), 678.

[9] *Z. anal. Chem.*, 1897, 36, 298. British Patent 20,225, 1896; *J.S.C.I.*, 1897, 16, 824. German Patent 89,598, 1896; *Z. angew. Chem.*, 1896, 9, 734.

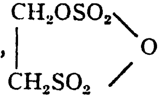
[10] *Chemische Industrie*, 1912, 35, 637; *Chem. Abs.*, 1913, 7, 243.

[11] U. S. Patent 1,919,618, July 25, 1933; assigned to Standard Alcohol Co.; *Chem. Abs.*, 1933, 27, 4818. Brooks, U. S. Patent 1,894,661, Jan. 17, 1933; assigned to Petroleum Chem. Corp.; *Chem. Abs.*, 1933, 27, 2572.

[12] *Compt. rend.*, 1913, 156, 557. *Ann. Chim.*, 1917, 8 (9), 246; *Chem. Abs.*, 1918, 12, 1444.

[13] *Gas J.*, 1919, 148, 718; *Chem. Trade J.*, 1919, 66, 61.

[14] *J.S.C.I.*, 1921, 40, 86T.

Our knowledge of the reaction between ethylene and sulphuric acid has been extended by the work of Plant and Sidgwick,[15] who studied the influence of various factors on the absorption of ethylene by acids of various concentrations without catalysts. Both the acid concentration and the temperature are important. Apart from decomposition, three successive stages were observed in the absorption process corresponding to (1) solution of ethylene in the liquid, (2) its reaction with sulphuric acid to yield ethylsulphuric acid, and (3) further interaction between ethylene and ethylsulphuric acid to yield diethyl sulphate. It was found that some diethyl sulphate was formed before all the sulphuric acid had been converted into ethylsulphuric acid, diethyl sulphate appearing after about 20 per cent of ethylene was absorbed. Considerable blackening occurred at 100° to 126° C. with 99 per cent acid, and absorption in oleum (containing 14 per cent sulphur trioxide) at these temperatures yielded large amounts of carbyl sulphate,  $\begin{matrix} CH_2OSO_2\diagdown \\ | \qquad\quad O \\ CH_2SO_2\ \diagup \end{matrix}$, a substance not hydrolyzable to alcohol.

A study of the reactions involved was made by Damiens,[16] who, with de Loisy, is responsible for the application of certain catalysts to the absorption process.[17] Damiens investigated the effects of various factors, namely, concentration of acid, efficient contact of gas with acid, partial pressure of the ethylene, temperature of absorption and the influence of catalysts. He found that, other factors being the same, the velocity of absorption in 99.5 per cent acid is 3 to 5 times greater than that in 95.5 per cent acid. Intensive agitation and good contact of gas with acids for a sufficient period of time favor rapid absorption. The velocity of absorption is diminished in roughly the same proportion as the partial pressure of ethylene. Raising the temperature from 25° to 60° C. increased the rate of absorption threefold. New and efficient catalysts for the reaction were found in cuprous salts, such as cuprous oxide, sulphate and chloride, all of which accelerate absorption. The addition of 5 per cent of cuprous oxide to 95 per

[15] *J.S.C.I.*, 1921, 40, 14T.

[16] *Compt. rend.*, 1922, 175, 585; *Bull. soc. chim.*, 1923, 33 (4), 71; *Chem. Abs.*, 1923, 17, 259.

[17] *Chim. Ind.*, 1923, 664, (Special Number, May 1923); *Chem. Abs.*, 1923, 17, 3318.

cent acid causes a rapid absorption of ethylene at 40° C. giving a 94 per cent yield of ethylsulphuric acid. Cuprous oxide dissolved in 98 per cent acid produces an identical reaction but continued introduction of ethylene yields diethyl sulphate. The proportion of diethyl sulphate is higher at lower temperatures, and Damiens considered that the following equilibrium was set up:

$$H_2SO_4 + (C_2H_5)_2SO_4 \rightleftharpoons 2C_2H_5HSO_4$$

Damiens observed the remarkable fact that sulphuric acid heated for a short time with cuprous oxide (until white fumes are evolved) and then cooled absorbed ethylene rapidly at 15° to 20° C. in the presence of mercury. The products consisted mainly of hydrocarbons from the polymerization of ethylene. To explain the catalytic activity of cuprous salts Damiens assumed the formation of complexes of the type $Cu_2SO_4 \cdot n(C_2H_4)$, which could either combine with the sulphuric acid to yield ethylsulphuric acid or with themselves to form higher hydrocarbons.

It is interesting to note that Böeseken and Max[18] separated a mixture of saturated and unsaturated hydrocarbons from the products of the absorption of ethylene in 93 to 95 per cent sulphuric acid containing 5 per cent of cuprous sulphate and 2 per cent of mercurous sulphate. The saturated hydrocarbons of low boiling point were probably paraffins.

Neumann[19] also recorded some experiments on the absorption of ethylene by sulphuric acid. The formation of ethylsulphuric acid increased with the concentration of the acid employed until 99 per cent was reached. Above that point the yield fell off sharply and carbyl sulphate made its appearance. Addition of catalysts increased the speed of absorption but at the same time produced undesirable by-products.

The search for other catalysts of the reaction between ethylene and sulphuric acid led to the conclusion by Gluud and Schneider[19a] that silver sulphate is an excellent material for this purpose. The addition of this compound (the most favorable concentrations being ½ to 1 per cent by weight) to sulphuric acid makes it possible to attain a much greater absorption at 40° C. than in ordinary acid at 80° C. The catalytic activity of silver sulphate as observed by Gluud and Schneider was also independently noticed by Lommell and Engelhardt,[20] who expressed the opinion that the reaction proceeds in two distinct stages, namely (1) the addition of ethylene to the silver salt which occurs rapidly even at room temperatures, and (2) the formation of ethylsulphuric acid which is slower but attains a satisfactory velocity at 40° C. Ethylene can be recovered unchanged from the initial addition compound by evaporation. Such addition compounds are also formed in aqueous solutions in the absence of sulphuric acid.

The description of an interesting process for the production of ethyl alcohol from ethylene in refinery gases has been given by Gerr, Pipik and Mezhebovskaya.[21]

> The gases used contained about 30 per cent unsaturates, and the underlying principle was the separation of ethylene by activated charcoal.[22] When the gases are passed through a large excess of charcoal the entire mixture is first absorbed, and then with

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[18] *Rec. trav. chim.*, 1929, **48**, 486; *Chem. Abs.*, 1929, **23**, 2929.

[19] *Gas und Wasserfach*, 1924, **67**, 1, 14, 53; *Chem. Abs.*, 1924, **18**, 2596.

[19a] *Ber.*, 1924, **57B**, 254.

[20] *Ber.*, 1924, **57B**, 848.

[21] *Azerb. Neft. Khoz.*, 1932, No. 2, 15; *Chem. Abs.*, 1932, **26**, 2853. See *Azerb. Neft. Khoz.*, 1932, No. 7, 88; *Chem. Abs.*, 1932, **26**, 5745; Geer and Melikova (*Azerb. Neft. Khoz.*, 1932, No. 7, 82; *Chem. Abs.*, 1932, **26**, 5745) regenerated the activated charcoal by treatment with steam at 200° to 360° C.

[22] For the theoretical basis of this use of activated charcoal, see Hill, *Petroleum World* (*Los Angeles*), 1929, **14**, No. 1, 101, 110; *Chem. Abs.*, 1929, **23**, 2285.

continued passage of the gas those hydrocarbons with the lower vapor pressures displace those with the higher vapor pressures. Saturated hydrocarbons are the least firmly held by the charcoal, and unsaturated hydrocarbons, containing double or triple bonds, are the most firmly held. Ethylene, the olefin of lowest molecular weight, is more easily displaced than any of its homologues.

An almost quantitative separation of ethylene from other unsaturated hydrocarbons could be obtained when a ratio of one liter of gas to 4 grams of charcoal was used. Absorption of the exit gas from the charcoal in sulphuric acid (d. 1.84) followed by hydrolysis and distillation yielded practically pure ethyl alcohol. For less pure or technical alcohol, the ratio could be decreased to 4 liters of gas to 5 grams of charcoal. The technical alcohol, however, always possessed a yellowish color and a slightly unpleasant odor [23] together with a slightly higher boiling point (78.6° C. at 760 mm.).

The gases were absorbed in concentrated sulphuric acid (d. 1.84) containing 1 per cent of silver, and the yield of alcohol (based on the raw gas) was about 13 to 15 per cent. Decreasing the quantity of silver catalyst materially decreased the yield of alcohol. The temperature of the acid during absorption was maintained at about 40° C. In the preparation of pure alcohol, the acid remaining after hydrolysis and distillation was transparent and clear, and the silver could be recovered either by electrolysis or by precipitation with hydrochloric acid. The recovery of the silver from the preparation of technical alcohol was complicated by the fact that the sludge of polymerization products formed during the reaction contained a large portion of the silver, and that some of the silver separated on the walls of the scrubber, leaving only a very small proportion dissolved in the acid layer. The sludge could be dissolved in nitric acid, from which the silver was recovered by precipitation.

Attempts were made to substitute an iron catalyst (the walls of the acid-scrubbing unit) for silver at a temperature of 80° to 95° C. The yield of alcohol was much lower, being about 8 per cent (based on the raw gas). On the basis of the ethylene content about 60 per cent utilization was obtained with the silver catalyst, and only 40 per cent with the iron catalyst.

The charcoal could be regenerated by treatment with superheated steam at 250° to 300° C. for several hours.

Dalin and Gutuirya [24] used the method of Gerr, Pipik and Mezhebovskaya in an investigation of alcohol manufacture from cracked gas. The product consisted of 90 per cent ethyl alcohol. However, only 5.5 to 6.2 per cent of the theoretical yield was obtained due to the faulty equipment and unsatisfactory regeneration of the charcoal.

The absorption of ethylene by ortho-, pyro-, and metaphosphoric acids was accelerated by the addition of cuprous oxide or silver sulphate.[25] Ethyl dihydrogen orthophosphate was formed with orthophosphoric acid and possibly also from pyrophosphoric acid.

The possibility of employing equal weights of chlorosulphonic acid and 100 per cent sulphuric acid for absorbing ethylene from coke-oven gas was examined by Traube and Justh.[26] The chlorosulphonic acid absorbs about 82 per cent of the theoretical quantity of ethylene yielding ethyl chlorosulphonate, which on hydrolysis is converted partly to alcohol and sulphuric and hydrochloric acids, and partly to ethyl chloride and sulphuric acid.

The effect of increasing the pressure of ethylene above atmospheric in the reaction with sulphuric acid was first investigated by Maimeri.[27] Experiments with 100 per cent sulphuric acid and 98 per cent ethylene at ordinary temperature showed that the amount of diethyl sulphate formed increased with increases in pressure, the absorption becoming ultimately so rapid that it was necessary to cool the reaction vessel. On dilution of the reaction product with iced water diethyl sulphate separated and was distilled under reduced pressure. The aqueous

[23] Bataafsche Petroleum Maatschappij (French Patent 744,119, 1933; *Chem. Abs.*, 1933, **27**, 3943; British Patent 393,152, 1932; *Brit. Chem. Abs.* **B**, 1933, 776) free alcohols of objectionable odor by dehydrating the alcohol-water polymer mixture before distillation, using such salts as anhydrous copper sulphate, calcium oxide or chloride. The mixture may also be treated with Edeleanu extract from mineral oil. See also Merley (U. S. Patent 1,873,005, Aug. 23, 1932; assigned to Doherty Research Co.; *Chem. Abs.*, 1932, **26**, 5964) for a method of dehydrating aqueous alcohols.

[24] *Azerb. Neft. Khoz.*, 1933, No. 3, 66; *Chem. Abs.*, 1933, **27**, 4211.

[25] Müller, *Ber.*, 1925, **58B**, 2105.

[26] *Brennstoff-Chem.*, 1923, 4, 150; *Chem. Abs.*, 1923, **17**, 3858. See also Traube, British Patent 147,543, 1920; *J.S.C.I.*, 1921, **40**, 74A.

[27] *Atti cong. naz. chim. Ind.*, 1924, 269; *Chem. Abs.*, 1925, **19**, 1402; *Giorn. chim. ind. appl.*, 1924, **6**, 533.

layer was neutralized with sodium hydroxide, evaporated to dryness, and the sodium ethyl sulphate extracted with alcohol. At 3.5 atmospheres pressure of ethylene the yields of diethyl sulphate and ethylsulphuric acid were 35 per cent and 51 per cent respectively (based on the sulphuric acid used), while at 10 atmospheres pressure the figures were 62 per cent and 30 per cent. The total yield of alcohol (based on sulphuric acid) was 57.5 per cent at 3.5 atmospheres and 76.7 per cent at 10 atmospheres, the latter being three times the best obtained by previous workers. Maimeri considered this method to be the most economical for the production of diethyl sulphate.

Thau and Bertelsmann [28] experimented with a coke-oven gas which had been washed with oil to remove benzol and freed of hydrogen sulphide. It was dried with sulphuric acid of 60° Bé and scrubbed with acid of the same strength, at temperatures varying from 60° to 135° C., in lead-lined iron containers filled with quartz lumps. The yield of alcohol diminished from 20.67 grams per cubic meter at 70° C. to 9.16 grams per cubic meter at 135° C. At 60° C. it was 19.32 grams per cubic meter. The ethylene content of the exit gas diminished from 0.85 per cent at 60° C. to 0.47 per cent at 135° C. As the temperature was increased considerable decomposition of the ethylsulphuric acid began to take place, sulphur dioxide being formed at 90° C. and some ether at 110° C.

The recovery of alcohol from the ethylene of coke-oven gas was discussed by Gluud, Schneider, and Keller,[29] who stated that the use of silver sulphate as a catalyst materially increases the probability of obtaining alcohol commercially from this source. It is essential however to eliminate the gaseous heavy hydrocarbons present in the raw gas and to reduce the quantity of water necessary for hydrolyzing the ethylsulphuric acid. Later Gerr and Popov [30] used the catalytic activity of silver sulphate for the production of alcohol from the ethylene present in cracking gas. A gas containing 54 per cent of paraffin hydrocarbons, 12.2 per cent of hydrogen, and 33.8 per cent of unsaturated hydrocarbons was passed over calcium chloride, then over wood charcoal (to remove the higher homologues of ethylene), and finally through an absorption tube, kept at 40° C. and containing glass beads or glass wool, in which a stream of a 1 per cent solution of silver sulphate in 94 per cent sulphuric acid absorbed the ethylene. In this manner 33.8 grams of alcohol were obtained from 300 liters of gas.

Behrens [31] described the preparation of ethyl alcohol, as well as acetaldehyde, from ethylene in the gases obtained by the destructive distillation of coal, lignite, peat, wood and similar materials. The gases are scrubbed with sulphuric acid, and the ethylsulphuric acid is either (1) hydrolyzed to yield alcohol, or (2) heated to give purified ethylene which can be oxidized catalytically to acetaldehyde.

DeLattre [32] proposed a method of treating coal-distillation gases by which they are passed, freed of the usual impurities, through concentrated sulphuric acid in the presence of vanadium or uranium oxides. The ethylsulphuric acid formed is converted into alcohol by hydrolysis. The residual gas containing methane and its homologues can be chlorinated photochemically and the chlorohydrocarbons then transformed into the corresponding alcohols by reaction with alkalies.

In 1919, Damiens, deLoisy and Piette [33] described a process for the manufacture of alcohol and ether from ethylene. The ethylene remaining in coal or coke-oven gas, after removal of ammonia, benzene and ethylene homologues, was absorbed in 66° Bé sulphuric acid (best at 100° to 120° C.) which contained one or more catalysts. Good results were obtained with acid containing 1 to 2 per cent of phosphoric acid anhydride, or 1 to 5 per cent of ferrous or cuprous sulphate. Before absorption of ethylene, the gas is dehydrated and freed from traces of higher reactive hydrocarbons. The acid, after absorption, is diluted and distilled to give either alcohol or ether or both. For example, when the absorbing acid was diluted with 60 per cent of its weight of water, distillation yielded a mixture of 22 per cent ether and 78 per cent alcohol. By diluting with 14 per cent of water and distilling, a mixture of 4 per cent ether and 96 per cent alcohol was obtained.

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[28] *Glückauf*, 1921, 189, 221; *Gas und Wasserfach*, 1921, **64**, 706; *Chem. Abs.*, 1922, **16**, 1309.

[29] *Ber. Ges. Kohlentechnik*, 1923, 210, 224; *Chem. Abs.*, 1924, **18**, 3470.

[30] *Neft. Khoz.*, 1926, 10, 88; *Chem. Abs.*, 1927, **21**, 2788.

[31] German Patent 275,049, 1913; *J.S.C.I.*, 1914, **33**, 807. See also Clausen, French Patent 625,379, 1926; *Brit. Chem. Abs.* **B**, 1928, 778.

[32] French Patent 468,244, 1914; *J.S.C.I.*, 1914, **33**, 953.

[33] British Patent 152,495, 1919; *J.S.C.I.*, 1920, **39**, 833A. U. S. Patent 1,599,119, Sept. 7, 1926; *Brit. Chem. Abs.* **B**, 1926, 1029.

In a description of the Skinningrove Iron Co.'s process, developed by Bury,[34] a number of details were presented. Cooled coke-oven gas is freed of hydrogen sulphide, and then of water by passing it through sulphuric acid. It is reheated in a heat exchanger and the ethylene absorbed in concentrated sulphuric acid at 60° to 80° C. in a series of scrubbers. The ethylsulphuric acid flows to a heat exchanger and thence to an alcohol still to which superheated steam is supplied. Ether may be recovered instead of alcohol or the solution oxidized electrolytically to yield acetic acid. Plant tests were said to have proved a recovery of 90 per cent of the ethylene (from gas containing 2 to 3.5 per cent), with 70 per cent as a safe working basis. Of the ethylene absorbed at least 70 per cent can be converted into absolute alcohol, an overall recovery of 50 per cent.

In making diethyl sulphate from ethylene and sulphuric acid, Curme[35] took advantage of the greater volatility of this compound. A rapid stream of ethylene is passed through sulphuric acid (93 per cent) at about 100° C. Ethylsulphuric acid is the initial product, but continued passage of the gas yields diethyl sulphate which is carried over with the stream of ethylene and condensed. After separation from some water (also carried over by the ethylene), diethyl sulphate is recovered in a substantially pure condition. Prolonged passage of the ethylene results in practically all of the sulphuric acid being converted into diethyl sulphate.

In the preparation of this same compound from ethylene and sulphuric acid, Maimeri[36] made use of pressures greater than atmospheric. Ethylene, free as far as possible from diluting gases, is treated under 15 atmospheres pressure at 55° to 65° C. (in the absence of catalysts) with 85 per cent sulphuric acid. Good stirring is necessary and the temperature must be maintained below 75° C. The reaction product is poured onto ice and separates into two layers, the lower of which consists of almost pure diethyl sulphate in a yield of 80 per cent of the theoretical.

The absorption of ethylene in dilute sulphuric acid (less than 80 per cent strength) at increased temperatures and pressures has been proposed by Joshua, Stanley and Dymock.[37] The reaction is carried out in the presence of materials (e.g., pumice, porcelain, or silica gel, or a compound of phosphoric acid and boric anhydride) which increase the surface contact of the reacting substances. A liquid surface extender, such as a refined mineral oil, or a combination of solid and liquid contact agents, may be employed simultaneously. The temperature at which absorption takes place determines the product of the reaction. For ex-

[34] British Patent 147,360, 1920; *Chem. Abs.*, 1920, 14, 3784.

[35] U. S. Patent 1,339,947, May 11, 1920; assigned to Union Carbide Co.; *Chem. Abs.*, 1920, 14, 2001.

[36] British Patent 215,000, 1924; assigned to Ledoga (Soc. anon.); *J.S.C.I.*, 1925, 44, 26B. See also Maimeri, *Atti. cong. naz. chim. ind.*, 1924, 269; *Chem. Abs.*, 1925, 19, 1402; *Giorn. chim. ind. Appl.*, 1924, 6, 533.

[37] Joshua and Stanley, British Patent 364, 221, 1930; *Brit. Chem. Abs.* B, 1932, 459; Joshua, Stanley and Dymock; British Patent 364,724, 1932; both patents assigned to The Distillers Co. Ltd.

ample, when ethylene is absorbed in dilute sulphuric acid at 90° C. and 50 to 100 atmospheres the main product is ethyl alcohol, while at temperatures above 100° C., at 50 atmospheres pressure, a mixture of ethyl ether and ethyl alcohol is obtained.[38] Brooks[39] sulphates ethylene or propylene by treating the gaseous olefin with 80 to 95 per cent sulphuric acid, under a pressure greater than 250 pounds per square inch, and at temperatures of 30° to 125° C.

A continuous method for the production of ether free from alcohol was described by Fritzsche.[40] In heating ethylsulphuric with water, ether vapors are produced along with the alcohol vapors. This mixture of ether and alcohol vapors is introduced into vessels containing ethylsulphuric, sulphuric acid or both. The alcohol vapors coming into contact with the ethylsulphuric acid are converted into ether. Bradley[41] recommended absorbing ethylene in concentrated sulphuric acid at about 140° C. Superheated steam, at a temperature higher than the boiling point of the acid, was then introduced into the mixture. This latter step keeps the acid strength constant during the distillation of the ether vapors, and permits re-circulation of the acid without further concentration.

Hydrolysis and distillation of ethylsulphuric acid may be accomplished by passing sulphuric acid containing ethylsulphuric acid and a stream of ammonia gas into a saturator in which dilute sulphuric acid is present. The dilute acid hydrolyzes the ethylsulphuric acid, and the heat of the reaction between ammonia and sulphuric acid is sufficient to effect distillation of the alcohol.[42]

Basore[43] developed a process having several features worthy of comment. The hydrolysis of ethylsulphuric acid by water to yield alcohol is relatively slow and requires a longer time than had hitherto been employed, and when the concentration of ethylsulphuric acid in the scrubbers is permitted to exceed 30 per cent (by weight) of the sulphuric acid, the subsequent dilution and treatment of the acid liquor yields considerable quantities of ether. Recognizing these facts, Basore preferred to discontinue the ethylene absorption when the ethylsulphuric acid content had risen to 10 to 20 per cent of the sulphuric acid and conducted the process as follows: The purified gas containing ethylene (e.g., coke-oven gas) is washed with sulphuric acid of 66° Bé, at a temperature of 70° to 80° C. When the ethylsulphuric acid content has risen to 10 to 20 per cent (by weight of the sulphuric acid), the acid is run into another vessel where a volume of water is added approximately 60 per cent of that of the sulphuric acid-ethylsulphuric acid mixture. This is heated for 60 minutes at a temperature of 100° to 120° C. to effect the complete hydrolysis of the ethylsulphuric acid, and is then distilled to yield alcohol.

A number of substances which catalyze the absorption of ethylene in sulphuric acid are mentioned by Damiens, de Loisy and Piette.[44] These consist of the lower oxides or salts of metals exhibiting more than one valence state, as for example iron, nickel, cobalt, cerium, manganese, chromium, copper, lead,

[38] Joshua and Stanley, British Patent 360,492, 1930; assigned to The Distillers Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 251.

[39] U. S. Patent 1,885,585, Nov. 1, 1932; assigned to Petroleum Chemical Corp.; *Chem. Abs.*, 1933, **27**, 1011.

[40] German Patent 88,051, 1895; *Chem. Zentr.*, 1896, **2**, 720.

[41] U. S. Patent 1,385,040, July 19, 1921; assigned to American Cellulose and Chemical Manufacturing Co.; *Chem. Abs.*, 1921, **15**, 3850. *Cf.* Duchange, U. S. Patent 1,674,891, June 26, 1928; assigned to Compagnie de Béthune; *Chem. Abs.*, 1928, **22**, 2951; British Patent 229,272, 1924; *J.S.C.I.*, 1925, 899B. See also I. G. Farbenindustrie A.-G., British Patent 362,593, 1930; *Brit. Chem. Abs.* **B**, 1932, 332; German Patent 544,284, 1930; *Chem. Abs.*, 1932, **26**, 2467.

[42] Compagnie de Béthune, British Patent 197,315, 1923; *J.S.C.I.*, 1923, **42**, 1198A; British Patent 229,272, 1924; *Chem. Abs.*, 1925, **19**, 3092.

[43] U. S. Patent 1,385,515, July 26, 1921; Reissue 15,211, 1921; *Chem. Abs.*, 1921, **15**, 3851. *Cf.* Kremann. *Monatsh.*, 1910, **31**, 245; *Chem. Abs.*, 1910, **4**, 2404.

[44] British Patent 180,988, 1922; *J.S.C.I.*, 1923, **42**, 440A; U. S. Patent 1,574,796, Mar. 2, 1926; *Chem. Abs.*, 1926, **20**, 1415; U. S. Patent 1,589,372, June 22, 1926; *Chem. Abs.*, 1926, **20**, 3015; U. S. Patent 1,599,119, Sept. 7, 1926; *Chem. Abs.*, 1926, **20**, 3460.

mercury, titanium or tin. Ferrous sulphate, cuprous chloride, cuprous oxide, and cuprous sulphate offer the advantage that they are insoluble and may be easily removed from the acid by filtration and used again. In the process alcohol is made from the ethylene of illuminating gas by passing the purified gas through a column (filled with pumice) in which it is washed by a stream of 66° Bé sulphuric acid, containing 5 per cent of cuprous oxide as catalyst, and maintained at a temperature of 35° to 40° C. In the presence of the cuprous salts diethyl sulphate begins to form at low temperatures (0° to 15° C.) when the concentration of ethylsulphuric acid is only 25.6 per cent instead of 75 per cent as normally.

The use of silver or silver salts as catalysts for the absorption of ethylene in 96 per cent sulphuric acid is suggested by Engelhardt, Lommel and Ossenbeck.[45] The silver may be employed in a colloidal state or as a salt or complex compound. The addition of 0.1 to 0:2 per cent of silver sulphate to 96 per cent acid is said to increase the volume of ethylene absorbed 13 times. Furthermore the rapidity of absorption is increased still more by raising the temperature or by the addition of small quantities of foam-producing or emulsifying materials (olive oil, castor oil, Turkey-red oil, chloroform, carbon tetrachloride or stearic acid). The use of foam-producing substances has also been suggested by the I. G. Farbenindustrie A.-G.[46]

In a process for the hydration of olefins McElroy[47] used sulphuric acid of catalytic strength, i.e., of a concentration sufficient to absorb the olefin and simultaneously give it up in the form of alcohol. He proposed to effect this reaction in a tower where the olefin gases are scrubbed countercurrently with a stream of acid. The concentration of the acid is adjusted so that it is less than catalytic strength at the end where the vapors leave the column and above catalytic strength at the other end where the gas first comes in contact with the acid. The temperature is regulated so that alcohol and water vapors are carried over with the gas stream. To replace water removed in this manner, continuous small additions of water or steam are made to the acid bath.

In a similar manner, Wibaut and Diekmann,[48] using an absorption tower, investigated the behavior of ethylene with acids of varying concentrations. The tower was heated electrolytically, allowing a means of controlling the temperature. Water vapor was added to the ethylene gas in order to keep the acid concentration constant. On the passage of 5 liters of ethylene using 65 per cent sulphuric acid at a temperature of 150° to 160° C., the distillate contained 0.21 gram of alcohol; 0.08 gram more alcohol was obtained on dilution and distillation of the acid. In a second experiment under the same conditions 4 per cent of the ethylene was converted. Using 55 per cent acid, only 0.01 gram of ethyl alcohol was found in the distillate. With acid of 70 per cent strength 0.32 gram of alcohol was present on dilution and distillation of the acid, no alcohol, however, being observed in the distillate. In this latter experiment only 3 liters of ethylene were passed through the reaction chamber.

The Compagnie de Béthune[49] described the production of ethylsulphuric acid by the absorption of ethylene in sulphuric acid of about 94 per cent concentration at 90° to 95° C. The ethylene or gas containing ethylene is circulated continuously through a drying tower and a sulphuric acid column containing Raschig rings or other packing materials and heated externally. A modification[50] consists in using hot concentrated sulphuric acid containing a constant proportion of ethylsulphuric acid (corresponding to an ethylene content of 11 to 18 per cent). It is stated that this mixture absorbs ethylene more rapidly than sulphuric acid alone. A further improvement[51] is realized by passing ethylene through a series of absorption vessels, maintained at successively higher temperatures. Each vessel is supplied independently with fresh sulphuric acid at such a rate as to maintain the concentration of ethylsulphuric acid at its optimum value for absorption purposes.

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[45] U. S. Patent 1,458,646, June 12, 1923; assigned to Farbenfabriken vorm. F. Bayer & Co.; *Chem. Abs.*, 1923, 17, 2587. See also British Patent 185,757, 1922; *Chem. Abs.*, 1923, 17, 771.

[46] German Patent 390,621, 1921.

[47] U. S. Patent 1,438,123, Dec. 5, 1922; *Chem. Abs.*, 1923, 17, 771.

[48] *Proc. Konig Akad. Wettens. Amsterdam*, 1923, **26**, 321; *J.C.S.*, 1923, **124**, 1049.

[49] British Patent 199,007, 1923; *Chem. Abs.*, 1924, **18**, 274.

Taveau[52] suggested conducting a mixture of olefins (such as cracking gas) through a series of absorption vessels containing sulphuric acid in increasing concentrations. The first two vessels are kept at a temperature of 30° C. and in these propylene and butylene are absorbed. In the last vessel ethylene is absorbed in 98 per cent acid at approximately 100° C.

The production of alcohol from the ethylene of coal gas by absorption in chlorosulphonic acid or fluorosulphonic acid has been described by Traube.[53]

The autocatalytic action of ethylsulphuric acid in accelerating the absorption of ethylene in sulphuric acid was utilized by Compton.[54] Ethylene is absorbed in sulphuric acid containing 20 to 90 moles of ethylene per 1000 moles of sulphur trioxide and the composition of the bath is held within the desired limits of concentration by frequent additions of fresh acid.

Bonn[55] liquefied coke-oven gases by cooling in stages and thereby obtained a mixture of liquefied methane and ethylene, which is separated by fractional distillation. The ethylene is purified and further treated by the usual methods for the production of ethyl alcohol or other ethyl derivatives.

While investigating the problem of the utilization of coke-oven gas as a source of ethyl alcohol, the Compagnie de Béthune[56] developed a process for separating a mixture of ethane and ethylene from that gas by liquefaction at —140° to —200° C. The distilled ethylene is absorbed in sulphuric acid and the residual ethane is thermally dehydrogenated at 600° to 800° C. to yield more ethylene. The utilization of the ethane of coke-oven gas is said to increase the yield of alcohol from distillation gases of coal by 30 per cent.

The Bataafsche Petroleum Maatschappij[57] used various catalysts for accelerating the absorption of ethylene in sulphuric acid, and for suppressing undesirable side reactions of the ethylene homologues. In one procedure various cyanogen compounds are suggested for this purpose, among them potassium ferro- and ferricyanides, tetraethyl ferrocyanide, sulphoferricyanic acid, sodium nitroprusside and prussoarsenite, and sodium ferrocarbonylpentacyanide. Other catalysts are compounds of the metals osmium, iridium, platinum, ruthenium, rhodium, palladium, copper, iron, cobalt or nickel.[58] Those metals or compounds which are insoluble in concentrated sulphuric acid may first be brought into a soluble form by converting them, for example, into soluble complex compounds with carbon monoxide or nitric oxide. It is also recommended that emulsifying agents or substances (ethyl alcohol, nitrobenzene, acetic acid or ether) which increase the solubility of ethylene in the acid be added. The metals of the platinum group themselves are active catalysts in a finely divided or colloidal form, as when precipitated on a carrier such as carbon black, silica gel or decolorizing clay.[59] The complete absorption of ethylene can be carried out by passing the gas, at a rate of 3 liters per hour into a solution of, for example, 5 grams of platinum dichlorodiphenylisonitrile in 100 cc. of 96 per cent sulphuric acid at a temperature of 160° C. About 90 per cent ethylene is absorbed when the rate is increased to 5 liters per hour.

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[50] Compagnie de Béthune, British Patent 221,512, 1923; *Chem. Abs.*, 1925, **19**, 832; German Patent 504,325, 1923; *Chem. Abs.*, 1930, **24**, 5306; see also Armstrong, *J.S.C.I.*, 1933, **52**, 251.

[51] Compagnie de Béthune, British Patent 273,263, 1927; *Brit. Chem. Abs.* **B**, 1927, 859.

[52] U. S. Patent 1,810,192, June 16, 1931; *Chem. Abs.*, 1931, **25**, 4557. Canadian Patent 258,227, 1924; *Brit. Chem. Abs.* **B**, 1927, 378; both patents assigned to The Texas Co.

[53] U. S. Patent 1,510,425, Sept. 30, 1924; *J.S.C.I.*, 1925, 4B.

[54] U. S. Patent 1,598,560, Aug. 31, 1926; assigned to Carbide and Carbon Chemicals Corporation; *Chem. Abs.*, 1926, **20**, 3460.

[55] German Patent 338,358, 1916; *J.S.C.I.*, 1921, **40**, 684A.

[56] British Patent 303,176, 1928; *Brit. Chem. Abs.* **B**, 1930, 358. French Patent 660,387, 1927; *Chem. Abs.*, 1930, **24**, 2760.

[57] French Patent 677,822, 1929; *Chem. Abs.*, 1930, **24**, 3247; French addition Patent 40,932, 1932; *Chem. Abs.*, 1933, **27**, 1359; British Patent 323,748, 1928; *Chem. Abs.*, 1930, **24**, 3247; British Patent 381,723, 1932; *Chem. Abs.*, 1933, **27**, 3943; Dutch Patent 25,123; *Chem. Abs.*, 1932, **26**, 1939.

[58] Bataafsche Petroleum Maatschappij, British Patents 336,603 and 336,604, 1929; *Chem. Abs.*, 1931, **25**, 1843.

The addition of some salts, particularly chlorides, to alcohol often results in the decomposition of both salt and alcohol. For example, aluminum chloride when added to either methyl or ethyl alcohol gives a violent evolution of hydrogen chloride. Ferric chloride does not react as rapidly, though at 50° C. its saturated solution yields chloroform and a dark red iron precipitate. Chloroform is also obtained slowly on boiling a saturated solution of cupric chloride in ethyl alcohol.[59a]

As pointed out, a number of outstanding attempts have been made, particularly by Fritzsche, Bury and Ollander, and Damiens and deLoisy, to apply the sulphuric acid process to large-scale production of ethyl alcohol from ethylene, apparently without much success. Commercial operation is hindered principally by the necessity of reconcentrating large quantities of diluted sulphuric acid to 95 to 97 per cent. It is reported that this difficulty has been overcome by the Compagnie de Béthune by neutralizing the diluted acid with ammonia and marketing the ammonium sulphate. So far as is known, the only firms actually manufacturing ethyl alcohol by this process are the Compagnie de Béthune and the Carbide and Carbon Chemicals Corporation.

SUMMARY

In the preceding discussion of the conversion of ethylene to alcohol by absorption in sulphuric acid and subsequent hydrolysis, the following salient features may be noted:

(1) The two principal reactions occurring during absorption are: first, the formation of ethylsulphuric acid, and second, at a later stage in the absorption operation, the production of diethyl sulphate.

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5SO_4H$$
$$C_2H_4 + C_2H_5SO_4H \longrightarrow (C_2H_5)_2SO_4$$

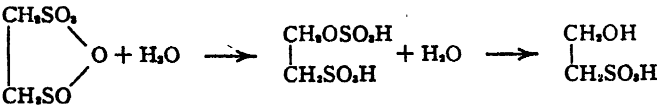
(2) The absorption of ethylene in sulphuric acid under ordinary conditions is rather slow but may be accelerated (a) by employing acid of very high concentration, (b) by increasing the reaction temperature, (c) by efficient agitation and intimate contact of acid with gas, (d) by adding such catalysts as silver sulphate or cuprous salts, and (e) by increasing the partial pressure of ethylene.

(3) The limiting concentration of acid is about 100 per cent or slightly less, since fuming acid favors the formation of carbyl sulphate, which hydrolyzes, not to alcohol, but to ethionic acid,[60] and then to isethionic acid, thus:

[59] Bataafsche Petroleum Maatschappij, British Patent 336,633, 1930; *Chem. Abs.*, 1931, **25**, 1843. Dutch Patent 27,237, 1932; *Chem. Abs.*, 1932, **26**, 5574; French Patent 695,707, 1930; *Chem. Abs.*, 1931, **25**, 2733; French Patent 696,561, 1930; *Chem. Abs.*, 1931, **25**, 2733.

[59a] Lloyd, Brown, Bonnell and Jones, *J.C.S.*, 1928, 658. See also Suknevitsch and Tschilingarian, *J. Gen. Chem. Russ.*, 1932, **2**, 783; *Brit. Chem. Abs.* **A**, 1933, 372.

[60] Salts of ester-like condensation products of ethionic and fatty acids have been suggested as detergents. Such materials are discussed in Chapter 46.



$$\begin{matrix} CH_2SO_2 \\ | \quad\; \diagdown \\ | \qquad O \\ | \quad\; \diagup \\ CH_2SO \end{matrix} + H_2O \longrightarrow \begin{matrix} CH_2OSO_3H \\ | \\ CH_2SO_3H \end{matrix} + H_2O \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2SO_3H \end{matrix}$$

(4) An increase in the temperature of absorption causes a notable increase in the velocity of reaction. Here again there is a practical limit, which appears to be in the neighborhood of 100° C., beyond which undesirable side reactions occur.

(5) All observers have stressed the importance of intimate contact for a sufficient time between the acid and gas. The methods for achieving intimate contact vary widely and comprise the use of porous or granular packing material, mechanical agitation, countercurrent washing over Raschig rings or other extended surfaces, and the addition of foam- and froth-producing materials and emulsifying agents, as well as organic solvents.

(6) It has been demonstrated beyond doubt that certain catalytic materials and increased pressures both increase the velocity of absorption.

(7) The hydrolysis of ethylsulphuric acid seems to be fairly rapid in the presence of water at 100° C. and involves little difficulty. Ammonia has been proposed as a neutralizing agent. Depending upon the degree of dilution of the ethylsulphuric acid, hydrolysis and distillation yield alcohol or ether or mixtures of the two. Dilution with about an equal volume of water favors high proportions of alcohol in the product.

DIETHYL SULPHATE

It is interesting to note that diethyl sulphate may be used as a commercial ethylating reagent in many organic reactions. According to Cade,[61] it has a boiling point of 96° C. at 15 mm., of 120.5° C. at 45 mm., and of 208° C. at 760 mm. (with decomposition); d^{19}_{4} 1.837, and melting point of —24.5° C.; is non-inflammable and non-toxic. Organic hydroxy-compounds react readily with this material to yield ethers, while inorganic salts convert it to the corresponding esters. With amines, diethyl sulphate gives either mono- or di-substituted derivatives. Thus, diethylaniline is obtained by the action of 1.4 moles of diethyl sulphate on 1 mole of aniline in the presence of 1.2 moles of calcium hydroxide. Other procedures, than those previously mentioned, for the manufacture of diethyl sulphate involve the reaction between ethyl alcohol and sulphuric acid or sulphur trioxide,[62] and the vacuum distillation of ethylsulphuric acid.[63]

HIGHER ALCOHOLS FROM ETHYL ALCOHOL

The catalytic conversion of ethyl alcohol to alcohols of higher molecular weight, such as butyl alcohol, has been proposed. One process for such a conversion is the passage of ethyl alcohol vapors at superatmospheric pressure (130 atmospheres or higher) and at temperatures of about 325° C. over a catalyst of magnesium oxide containing a small proportion of copper oxide.[64] In another procedure,[65] ethyl alcohol vapors together with hydrogen are conducted at atmospheric pressure and a temperature of 200° C. or higher over a magnesium oxide catalyst activated by the oxides of metals such as lead, nickel, cobalt, silver, uranium, tungsten, copper and others. The catalyst may be stabilized by the addition of aluminum hydroxide, stannic acid, silica gel or wood charcoal. The products consist not only of n-butyl but also hexyl and octyl alcohols, acetaldehyde, and some butyric and crotonic aldehydes. By passing a mixture of ethyl and methyl alcohol and hydrogen over these catalysts a product is obtained containing methylethylcarbinol, propyl, isobutyl, butyl, hexyl, heptyl, octyl and nonyl alcohols.[66] Joshua, Stanley and Dymock[67] pass a mixture of ethyl and butyl alcohols and hydrogen over a mixed catalyst of aluminum, uranium, and thorium oxides with copper, silver, nickel or chromium. The main product is hexyl alcohol.

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[61] *Chem. Met. Eng.*, 1923, 29, 319. *Cf.* Wachtel, *Z. exp. Path. Ther.*, 1920, 21, 1; *Chem. Abs.*, 1921, 15, 120.

[62] Lilienfeld, British Patent 143,260, 1920; *J.S.C.I.*, 1921, 40, 322A. Bader, U. S. Patent 1,484,249, Feb. 19, 1924; assigned to H. Dreyfus; *J.S.C.I.*, 1924, 43, 314B. Adamson, U. S. Patent 1,399,238, Dec. 6, 1921; assigned to General Chemical Co.; *J.S.C.I.*, 1922, 41, 79A. The production of dialkyl sulphates by reaction of olefins and sulphuric acid was also described by Deanesly, British Patent 363,028, 1930; *Chem. Abs.*, 1933, 27, 1421; Canadian Patent 310,439, 1931; *Chem. Abs.*, 1931, 25, 3014; French Patent 704,876, 1930; *Chem. Abs.*, 1931, 25, 4557; French Patent 718,943, 1931; *Chem. Abs.*, 1932, 26, 3261; all patents assigned to Bataafsche Petroleum Maatschappij.

[63] British Cellulose and Chemical Manufacturing Co., Ltd., British Patent 175,077, 1922; *J.S.C.I.*, 1922, 41, 309A.

[64] Wibaut, U. S. Patent 1,910,582, May 23, 1933; *Chem. Abs.*, 1933, **27**, 3951; British Patent 336,811, 1930; *Chem. Abs.*, 1931, **25**, 1844; French Patent 695,765, 1930; *Chem. Abs.*, 1931, **25**, 2739; German Patent 545,849, 1930; *Chem. Abs.*, 1932, **26**, 3521; all patents assigned to Bataafsche Petroleum Maatschappij. In the presence of dehydration catalysts such as aluminum oxide, thorium oxide, or aluminum sulphate at 400° C. under pressure, the alcohols are said to be transformed to the corresponding ethers (Bataafsche Petroleum Maatschappij, British Patent 332,756, 1929; *Chem. Abs.*, 1931, **25**, 302; French Patent 701,335, 1930; *Chem. Abs.*, 1931, **25**, 4011).

[65] Fuchs and Querfurth, British Patent 364,134, 1930; *Brit. Chem. Abs.* **B**, 1932, 459.

[66] Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, British Patent 381,185, 1932; *Chem. Abs.*, 1933, **27**, 3943. See also French Patent 42,154, 1933; *Chem. Abs.*, 1933, **27**, 4813; addition to 722,050; *Chem. Abs.*, 1932, **26**, 4062.

[67] British Patent 393,267, 1931; assigned to British Industrial Solvents, Ltd.; *Brit. Chem. Abs.* **B**, 1933, 777.

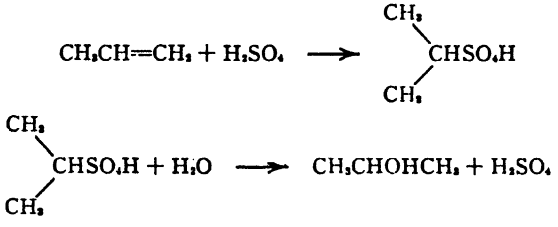
Chapter 14

Reaction Between Sulphuric Acid and Propylene. Production of Isopropyl Alcohol

The reaction between ethylene and concentrated sulphuric acid results almost exclusively in the esterification of ethylene with the production of ethylsulphuric acid and subsequently of diethyl sulphate. Propylene, however, reacts much more rapidly and easily with sulphuric acid and therefore less concentrated acid and lower temperatures may be employed. One can even separate ethylene and propylene by using sulphuric acid of the proper concentration. The simple esterification of propylene is complicated by polymerization and decomposition of the polymers as the predominating reactions at higher temperatures. Diluted acid is customarily used as concentrated acid favors the formation of polymers.

In the following pages a résumé is given of the most important work on the reactions of propylene and sulphuric acid, the subject being treated with special reference to the production of isopropyl alcohol. Since many of the industrial processes for making alcohols from olefins are concerned with mixtures of ethylene homologues found in the gas from cracking plants, some of the methods here given are also applicable to the production of the higher secondary and tertiary alcohols, a subject more fully discussed in a subsequent chapter.

It has long been known that propylene can be converted into isopropyl alcohol by reaction with sulphuric acid followed by hydrolysis of the resulting isopropylsulphuric acid, as follows:



$$CH_3CH{=}CH_2 + H_2SO_4 \longrightarrow (CH_3)_2CHSO_4H$$

$$(CH_3)_2CHSO_4H + H_2O \longrightarrow CH_3CHOHCH_3 + H_2SO_4$$

Yet the published work dealing with these reactions is not very extensive. Berthelot carried out some investigations on the production of secondary alcohols by this method. As early as 1855 we find his publications, one dealing with the absorption of propylene in sulphuric acid followed by the distillation of the acid compound mixed with water[1]; and others discussing the use of 98 per cent sulphuric acid[2] and the transformation of the alcohol, produced from olefin-containing gas and sulphuric acid, into ether.[3] Later Berthelot[4] investigated the velocity of and the effect of temperature on the absorption of propylene in sulphuric acid, and the formation of polymerization products during the subsequent distillation with water. He observed that sulphuric acid hydrate absorbed two hundred times its volume of propylene and that on mixing with water and distilling, an alcohol with a boiling point of 82° C. was obtained.

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[1] *Jahresber. Fortschr. Chem.*, 1855, 611; *Ann. Chim. Phys.*, 1894, (7) 4, 102; see also *Compt. rend.*, 1894, 118, 1009.

[2] *Ann. Chim. Phys.*, 1855, (3), 43, 385.

[3] *Compt. rend.*, 1855, 40, 102.

[4] *Ann. Chim. Phys.*, 1895, (7), 4, 105.

Plant and Sidgwick[5] noted that the rate of absorption of propylene in sulphuric acid was very much greater than that of ethylene. On passing propylene through 97 per cent sulphuric acid at 25° C., a 50 per cent increase in weight took place in two hours. Apart from the production of isopropylsulphuric acid and isopropyl sulphate there was also formed a quantity of colorless oil boiling from 55° to 155° C. at 30 mm. Analysis of this oil together with the fact that it appeared to react with metallic sodium led Plant and Sidgwick to believe it was a mixture of higher secondary alcohols produced by the action of sulphuric acid on the polymers of propylene. This conclusion, however, has been contested by Ormandy and Craven.[6]

A series of measurements of the relative rates of absorption of gaseous olefins in sulphuric acids of various concentrations has been reported by Davis and Schuler.[7] Their results for the absorption of ethylene in concentrated acid showed: (a) the film of acid on the glass walls of a pipette absorbed as much per unit area as the surface of the acid itself, (b) the absorption rate was not greatly changed by renewal of the surfaces or by the agitation in the liquid caused by rotation of the pipette, and (c) the rate was hardly affected by a nine-fold change in the volume of the acid. In view of these results Davis and Schuler concluded that the reaction between ethylene and sulphuric acid takes place entirely in a very thin film at the surface. These investigators showed that the absorption rate of propylene always remained about 300 times that of ethylene for acid concentrations of 80 per cent and higher, this in spite of the fact that the absolute values for the rates of absorption changed almost 200-fold over the range of acid concentrations employed.

Ormandy and Craven in a series of publications[8] have brought forward much evidence to show that the interaction of olefin hydrocarbons with sulphuric acid produces not only alcohols, alkylsulphuric esters, and olefin polymers, but a remarkable splitting of the olefin polymers takes place yielding considerable quantities of paraffin hydrocarbons. Empirically the reaction leading to the production of open chain paraffins is written by Ormandy and Craven as:

$$3xC_nH_{2n} \longrightarrow 2C_{nx}H_{2nx+2} + C_{nx}H_{2nx-4}$$

Thus it was found that on bubbling gaseous olefins, of 3 or more carbon atoms per molecule, through 98 per cent sulphuric acid at 25° C. separation of colorless oils occurred immediately. Dilution of the acid layer yielded oily products referred to as acid wash oils and the residual aqueous acid was fractionated to recover the free alcohols. The separated oils possessed physical properties and yielded analytical results which showed that they consisted of mixtures of open chain paraffins. The acid wash oils were unsaturated, had a high refractive index, and tended to darken on exposure to air. Apparently Ormandy and Craven considered that triolefins are present in these oils. Some results obtained with propylene are noteworthy. Propylene was passed into 98 per cent acid below 25° C. until about 12 per cent by weight was absorbed. The products of the reaction contained 46.7 parts of free oil, 44.7 parts of acid wash oils, and 5.2 parts of

[5] *J.S.C.I.*, 1921, **40**, 17T.
[6] *J.S.C.I.*, 1928, **47**, 317T.
[7] *J.A.C.S.*, 1930, **52**, 721.
[8] *J. Inst. Pet. Tech.*, 1927, **13**, 311, 844; *J.S.C.I.*, 1928, **47**, 317T; 1929, **48**, 293T.

isopropyl alcohol per 100 parts of olefin absorbed. The absorption of propylene was studied in some detail and the result established that one molecule of sulphuric acid absorbs at least three molecules of propylene over and above that which goes to form hydrocarbons. Thus by absorbing propylene in 98 per cent acid below 25° C. for 17 hours 1.10 moles of propylene (per mole of sulphuric acid) were recoverable as hydrocarbons and in addition 3.78 moles of propylene were otherwise absorbed. In an experiment in which propylene was absorbed in 80 per cent sulphuric acid, a 10 per cent increase in weight took place after 14 hours bubbling and 24 per cent of the propylene was converted into paraffins and 62 per cent into isopropyl alcohol. This experiment clearly confirmed the findings of Ellis and his co-workers as to the desirability of using as dilute acid as possible, consistent with sufficiently rapid absorption, to avoid undesirable side-reactions in the manufacture of isopropyl alcohol from propylene.

By saturating 98 per cent sulphuric acid with propylene at as low a temperature as the melting point of the mixture would permit, Ormandy and Craven[9] were able to prepare diisopropyl sulphate, a colorless liquid melting at —19° C., d^{15} 1.1155, and n^{16}_{D} 1.4121, which decomposes rapidly when warmed to 55°-60° C. This instability of diisopropyl sulphate was also noted by Bert,[10] who prepared the substance by the action of sulphuryl chloride on the sodium derivative of isopropyl alcohol. Medvedev and Alekseeva[11] found that on removing all traces of mineral acids the diisopropyl sulphate was quite stable. It could be distilled *in vacuo* without appreciable decomposition and kept unchanged for several days over calcium chloride.

Attempts have been made by a number of workers to hydrate propylene to isopropyl alcohol with water in the presence of catalysts. On passing a stream of propylene, to which a quantity of steam had been added at 125° to 130° C., countercurrent to a stream of 45 per cent sulphuric acid or of a concentrated aqueous solution of benzenesulphonic acid, Wibaut and Diekmann[12] obtained some isopropyl alcohol on cooling the exit gases. By carefully adjusting the proportion of steam in the ingoing gases it was possible to maintain the concentration of the acid at a constant value, and under these conditions the acid functioned as a hydrating catalyst. A large proportion of the propylene, however, was decomposed by the sulphuric acid and separation of carbon and formation of sulphur dioxide took place.

Comparatively few experimental details have been published on the conditions necessary for the production of good yields of isopropyl alcohol from propylene. The conclusion of Ormandy and Craven that it is difficult to prepare isopropyl alcohol by the use of sulphuric acid without losing 30 per cent or more by polymerization was contested by Norris and Davis,[13] who stated that carefully controlled tests both in the laboratory and in a semi-commercial plant have shown that it is possible to obtain almost quantitative yields of isopropyl alcohol from propylene using very concentrated sulphuric acid.

INDUSTRIAL PRODUCTION OF ISOPROPYL ALCOHOL

The production of tremendous volumes of gaseous and low-boiling liquid olefins during commercial cracking operations has greatly stimulated the industrial use of these olefins as raw materials for the manufacture of secondary and even of

[9] *J.S.C.I.*, 1930, 49, 362T; *cf.* Levaillant, *Compt. rend.*, 1929, 188, 261; *Chem. Abs.*, 1929, 23, 4669.
[10] *Bull. soc. chim.*, 1925, 37, 1252; *Chem. Abs.*, 1926, 20, 1793.
[11] *Ber.*, 1932, 65B, 131.
[12] *Proc. Konig. Akad. Wetensch. Amsterdam*, 1923, 26, 321; *Chem. Abs.*, 1923, 17, 3858.
[13] *J.S.C.I.*, 1929, 48, 70T.

tertiary alcohols. The first commercial production of isopropyl alcohol was undertaken during the War period by the Melco Chemical Co. operating the Ellis process.[14] The still gases obtained in the cracking process were freed of hydrogen sulphide and water vapor, and the olefins then absorbed by passing the gases through 87 per cent sulphuric acid (sp. gr. 1.8) at 15° to 20° C., a rise in temperature being avoided by refrigeration. The undissolved gases at that time were used for fuel. When the specific gravity of the acid solution reached 1.4, the product was diluted with 4 volumes of water, and the polymers which separated were withdrawn. The diluted acid was next distilled, and the isopropyl alcohol obtained as a 20 per cent aqueous mixture. The crude product was further concentrated by distillation, yielding a constant-boiling mixture of isopropyl alcohol and water, containing 91.09 per cent alcohol by volume.

During the World War when acetone was in great demand for making airplane "dope", the Bureau of Aircraft Production took over the Melco plant and thoroughly studied the problem of making acetone from the isopropyl alcohol by catalytic oxidation in the presence of copper, or other metals, and by its dehydrogenation in contact with heated zinc, copper or brass. The enormous wartime need of acetone undoubtedly could have been satisfied in this manner had not the termination of the War soon thereafter eliminated the demand. Later the Standard Oil Co. of New Jersey obtained the rights to the Ellis process, and for many years has been producing both 91 per cent and anhydrous isopropyl alcohol in large quantities at its Bayway refinery.

Since that time the higher secondary and tertiary alcohols have been added to the list of commercial organic chemicals. By far the most important production of such alcohols has been that carried out under the auspices of the Standard Oil Co. of New Jersey, who later organized the Standard Alcohol Co. to continue this development.[15]

Ellis [16] has developed a process for producing alcohols from cracking gas which consists in bringing the gas in contact with sulphuric acid of 1.8 specific gravity at fairly low temperatures (below 20° C.) in the presence of a nonreactive liquid absorbent for the gases immiscible with sulphuric acid. This process results in the absorption of propylene and higher olefins. The resulting acid liquor, when it has reached a specific gravity of 1.3 to 1.4, is hydrolyzed with water to yield a mixture of isopropyl alcohol and higher alcohols. The acid liquor may also be used to make acetates or other esters of the secondary alcohols by reaction with the sodium salt of the appropriate aliphatic acid. The ethylene present in the cracking gas may afterwards be absorbed in more concentrated acid (100 per cent) at 60° to 70° C., also in the presence of a liquid diluent (for example, molten paraffin wax), to yield ethylsulphuric acid.

Two other processes for the manufacture of alcohols by sulphuric acid treatment of olefins have been developed by Ellis.[17] In the first, cracked gasoline boiling up to 110° C. is agitated for 3 hours with sulphuric acid of 1.8 specific gravity, the temperature being kept low by cooling. The mixture is then allowed to stand and the acid extract, separating as a bottom layer, is drawn off, diluted with water, and distilled with steam to yield a mixture of water-insoluble alcohols. About 25 per cent of these alcohols boil up to 115° C., 55 per cent from 115° to 150° C., and 20 per cent above 150° C. The upper layer of hydrocarbons may

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[14] *Chem. Met. Eng.*, 1920, 23, 1230; *J.S.C.I.*, 1921, 40, 89R.

[15] *Nat. Pet. News*, 1932, 24, No. 49, 25. The Standard Alcohol Co. was formed in 1932 to continue operations under the Ellis process and to include certain improvements of Davis and others. (See also Chapter 16.)

[16] U. S. Patent 1,464,153, Aug. 7, 1923; *Chem. Abs.*, 1923, 17, 3248.

[17] Ellis *et al.*, U. S. Patents 1,486,646, March 11, 1924, and 1,486,647, March 11, 1924.

Courtesy Standard Alcohol Co.

FIG. 23.—General View of

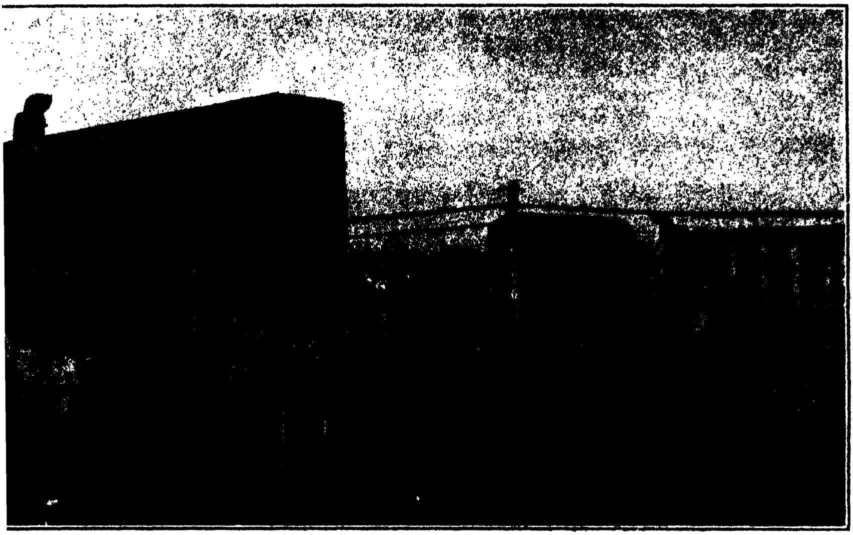
be retreated with sulphuric acid to extract the residual olefins, leaving a mixture of saturated hydrocarbons only. The second process is concerned with the production of acid extract and alcohols from the gaseous products of cracking. By washing the cracking gas in an absorption tower, packed with contact material, with sulphuric acid of 1.8 specific gravity at a temperature below 40° C., there is obtained an acid liquor, the major portion of which consists of sulphated derivatives of olefins (mixture of alkylsulphuric acids) of more than two carbon atoms, predominantly derivatives of propylene. Since the extent of polymerization depends mainly on the time of exposure of the olefin to sulphuric acid, on the temperature, and on the concentration of the acid, too high temperatures and too concentrated acids are to be avoided. The sulphated material, as formed, should be immediately mixed with water to check any sulphonation or polymerization. The alcohols may be removed from the dilute acid by distillation with steam.

In order to avoid excessive polymerization of propylene caused by too high an acid concentration or temperature, Brooks and Cardarelli[17a] kept the partial pressure of propylene in excess of 50 pounds per square inch. Best results were obtained with the partial pressure in excess of 100 pounds per square inch with an acid concentration of 75 to 80 per cent and a temperature of 10° to 30° C., or with an acid concentration of 70 to 75 per cent and a temperature of 40° C.

In the absorption of propylene, and its homologues present in cracking gas, in sulphuric acid of 1.8 specific gravity at about 20° C., protracted contact between the gas and the acid, as previously noted, is undesirable.[18] Generally speaking 3 to 10 hours circulation of each batch of acid is sufficient, according to Ellis,[18] to give good yields of alcohol, while the passage of the gas for 24

[17a] U. S. Patent 1,919,617, July 25, 1933; assigned to Standard Alcohol Co.; *Chem. Abs.*, 1933, 27, 4818.

[18] U. S. Patent 1,594,823, Aug. 3, 1926. *Cf.* British Patents 146,956, 1920; 146,957, 1920; 173,538, 1921; all assigned to S. B. Hunt, trustee.



Isopropyl Alcohol Plant.

to 48 hours through a single batch of acid is likely to yield little or no alcohol. Introduction of the gas normally is continued until the specific gravity of the acid liquor has fallen to 1.3 to 1.4.[19]

Ellis[20] also suggested adding sulphuric acid of about 1.8 specific gravity gradually to cracked petroleum containing both olefins and saturated liquid hydrocarbons, separating the acid layer by settling and then hydrolyzing it to yield alcohols. Before hydrolysis, the acid layer can be used for the treatment of additional olefin-containing material.

The use of an inert liquid, such as petroleum oil, agitated with the absorbing acid has been recommended by Mann and Williams.[21] Gaseous propylene is readily soluble in such a petroleum liquid and by employing it, better contact between the acid and propylene is secured. This procedure also reduces the polymerizing effect of the acid on propylene.

Mann[22] proposed the removal of small quantities of oil from isopropyl alcohol by bringing the liquid into intimate contact with sawdust. Lebo[23] suggested separating isopropyl alcohol from other admixed alcohols by adding a small quantity of benzene to the crude isopropyl alcohol before distilling. The benzene forms a low-boiling mixture with the isopropyl alcohol and this mixture can be separated subsequently into benzene and isopropyl alcohol by distillation. It has also been reported by Lebo[24] that isopropyl, butyl and amyl alcohols may be

[19] Incidentally it is proposed to increase the yield of olefin by thermally dehydrogenating the paraffin hydrocarbons (remaining after the first absorption) at 500°-700° C. under a pressure of 7 to 8 pounds less than atmospheric. The resulting olefins are absorbed in acid of sp. gr. 1.8 to yield isopropyl and higher alcohols.

[20] U. S. Patents 1,365,044 and 1,365,046, Jan. 11, 1921.

[21] U. S. Patent 1,365,043, Jan. 11, 1921; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1921, **15**, 944.

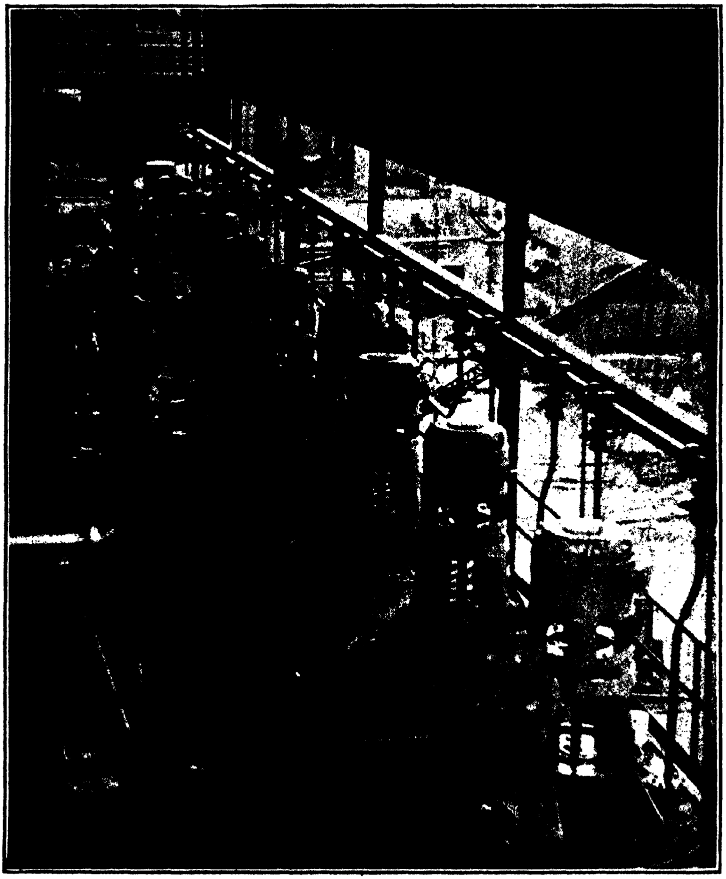
[22] U. S. Patent 1,413,864, Apr. 25, 1922; assigned to Standard Oil Development Co.; *J.S.C.I.*, 1922, **41**, 438A.

[23] U. S. Patent 1,422,583, July 11, 1922; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1922, **16**, 3093.

[24] U. S. Patent 1,870,815, Aug. 9, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1932, **26**, 5578.

freed from certain impurities, particularly sulphur compounds, by first digesting the crude product with less than 2 per cent by volume of 40° Bé. nitric acid, then neutralizing the acid with an alkali, and finally distilling the alcohol from the neutralized mixture.

In the Ramage[25] process the low-boiling fractions of cracked distillates, containing both olefins and aromatics, are treated with 60° to 66° Bé. sulphuric acid, cooling if necessary to prevent loss of volatile hydrocarbons. For example, a fraction of cracked gasoline, boiling between 70° and 95° C., is treated with 25 per cent by weight of 66° Bé. sulphuric acid with thorough agitation. After the addition of the acid is completed, a volume of water, equal to about 10 times the volume of acid, is added and the mixture then allowed to separate into two layers. An alkali, such as sodium carbonate, may be dissolved in the water. This alkali



Courtesy Standard Alcohol Co.

FIG. 24.—Agitator Motors in an Isopropyl Alcohol Plant.

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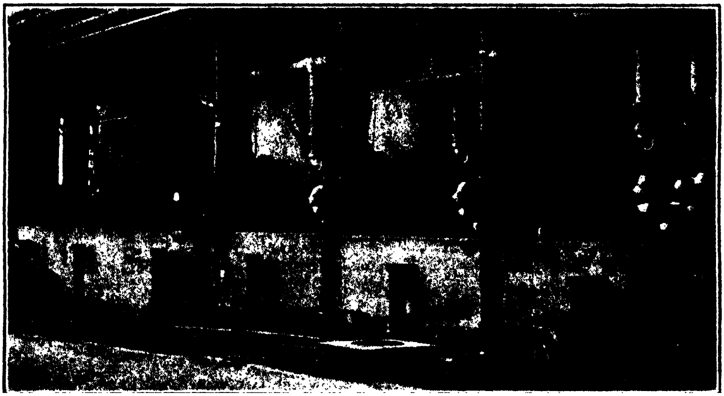
[25] U. S. Patent 1,407,770, Feb. 28, 1922; *Chem. Abs.*, 1922, 16, 1663.

neutralizes the acid and assists in the hydrolysis of the alkylsulphuric acid derivative formed. The upper, or oil layer, is withdrawn and separated into various fractions by distillation. The lower-boiling fractions are said to consist largely of alcoholic and aromatic bodies, the intermediate fractions of xylol and terpenes, and the high-boiling fraction (above 275° C.) is a lubricating oil, very probably containing largely polymerization products of the olefins.

In another process developed by Ramage[26] a mixture of olefin and aromatic hydrocarbons, having a boiling range of 20° to 150° C. obtained by the cracking of petroleum oil, is treated with about 20 per cent by volume of 66° Bé. sulphuric acid, the temperature being maintained below 40° C. Upon settling the mixture forms two layers: (1) a supernatant mixture of liquid hydrocarbons mostly of an aromatic nature (which can be fractionated and the lower fractions nitrated to yield nitro-compounds) and (2) an acid sludge, consisting of a mixture of sulphuric acid derivatives of the lighter olefins, chiefly those up to and including $C_{10}H_{20}$, and acid resins derived from the higher olefins. The acid sludge is diluted with an equal volume of water, agitated, and allowed to settle, yielding (1) an aqueous solution of various alcohols which is distilled to concentrate the alcohols, and (2) a tarry layer containing acid resins. The latter is extracted with 10 per cent caustic soda solution from which the acid resins may be precipitated by acidulation.



Courtesy Standard Alcohol Co.

FIG. 25.—Steam Stills in an Isopropyl Alcohol Plant.

A process described by McElroy[27] is intended to convert the gaseous olefins present in oil gas into alcohols by what may be virtually a catalytic hydration in the presence of sulphuric acid. Olefin gas is brought into contact with sulphuric acid of such a concentration and at such a temperature that the olefin is absorbed and immediately given up in the form of alcohol, which is carried forward in the gas stream and condensed. The olefin gas first passes through a preliminary scrubber where it comes in contact with dilute sulphuric acid (1 part of acid and 3 parts of water) which removes the more easily polymerized olefins. The olefin gas then passes from the top of the preliminary scrubber to the base of the reaction chamber, which is maintained at a temperature of 80° to 100° C. by a heating packet. Dilute sulphuric acid is fed into the top of the reaction chamber and flows down through a customary bubble tower arrangement to secure intimate contact with the ascending stream of olefin gas. As the temperature of the reaction chamber is high enough to cause the evaporation of some water, the acid withdrawn from its base is much more concentrated than that entering the top. This concentrated acid, together with any dissolved olefins, is pumped back to the acid tank at the top of the reaction chamber, where it is diluted with water to the original strength. The olefin gas passing up through the chamber is absorbed by the acid, forming alkyl acid derivatives. These are immediately hydrolyzed to the corresponding alcohols, which in turn are vaporized. The alcohol vapors together with water vapor pass out of the top of the reaction chamber into an accessory column still. Part of the water vapor is condensed in a preliminary condenser and returned to the reaction chamber. The uncondensed gases are led to a final condenser to yield a condensate containing 10 to 15 per cent or more of alcohol, which may be further rectified.

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[26] U. S. Patent 1,483,835, Feb. 12, 1924; *Chem. Abs.*, 1924, 18, 1194.
[27] U. S. Patent 1,438,123, Dec. 5, 1922; *Chem. Abs.*, 1923, 17, 771.

The Compagnie de Béthune[28] proposed the conversion of the ethylene homologues (principally propylene) present in coke-oven gas into the corresponding alcohols by treatment with about 90 per cent sulphuric acid at 18° C., followed by hydrolysis of the alkylsulphuric acid and distillation of the alcohols.

The successive removal of olefins in the gases from cracking operations is reported by Taveau.[29] The olefin-containing gases are passed countercurrent to sulphuric acid through a series of reaction chambers. By using acids of successively higher concentrations and by raising the temperature, the removal of the olefinic gases in stages is accomplished. For example, the cracking gases are first brought into contact with 65-66 per cent sulphuric acid at 30° C., under which conditions isobutylene is absorbed. The residual gases are next treated with 85 per cent acid, at the same temperature, which removes the remaining isomeric butylenes. Acid of about 94 per cent concentration, in the following series of reaction chambers at 30° C., reacts with the propylene, and 98 per cent acid at 100° C. used in the last chambers absorbs ethylene. The reactive acid liquor from each step is hydrolyzed, or otherwise treated, as soon as possible to avoid unnecessary polymerization.

Another process suggested for the separation of olefins from gaseous mixtures consists in treating the mixture with sulphuric acid in three stages.[30] The concentration of the acid for the first stage is less than 65 per cent, for the second stage, 78 to 82 per cent, and for the third stage, above 90 per cent. For the first two stages the temperature is kept at 32° to 49° C. The addition of an absorption oil to the acid assists by promoting more intimate contact between the acid and olefins and by reducing polymerization of the olefins.

The fractional extraction of olefins from cracking gas at lower temperatures, 3° C. or less, has been reported.[31] At such temperatures sulphuric acid of not less than 75 per cent strength removes isobutylene and the amylenes, while propylene and the normal butylenes are absorbed by acid of not less than 88 per cent strength.

An apparatus for the absorption of olefins present in petroleum distillation gases has been described by Mann.[32] The absorbing liquid may be, for example, sulphuric acid of 1.8 specific gravity mixed with a saturated paraffin oil in the

[28] French Patent 636,651, 1926; *Brit. Chem. Abs.* **B**, 1930, 500.

[29] U. S. Patent 1,810,192, June 16, 1931; assigned to The Texas Co.; *Chem. Abs.*, 1931, 25, 4557.

[30] Buc, British Patent 340,098, 1929; *Brit. Chem. Abs.* **B**, 1931, 192; French Patent 684,567, 1929; *Chem. Abs.* 1931, 25, 2733. Both patents assigned to Standard Oil Development Co.

[31] Markovich and Pigulevskii, Russian Patent 25,599, 1932; *Chem. Abs.*, 1932, 26, 5312.

[32] U. S. Patent 1,654,181, Dec. 27, 1927; assigned to S. B. Hunt; *Brit. Chem. Abs.* **B**, 1928, 249.

proportion of 1 part of acid to 5 parts of oil, and gas is supplied to the absorber under a pressure of 4 to 5 atmospheres.

A plan offered by Pilat, Piotrowsky and Winkler[33] to produce propyl and butyl, as well as higher, alcohols from the olefins of gases obtained in coal distillation or from the cracking of oil utilizes numerous features described above. The gases, after being desulphurized, dehydrated and freed of gasoline, are absorbed under pressure at temperatures below 20° C. in 70 to 90 per cent sulphuric acid. A well-refined oil, such as solar oil, may be mixed with the sulphuric acid.

Another procedure involves using dilute sulphuric or hydrochloric acids (concentration less than 3 moles per liter) at high temperatures and maintaining the gaseous olefins under high pressures.[34] For example, propylene or a higher olefin at a partial pressure greater than 10 atmospheres is forced into the dilute acid at a temperature of 150° to 222° C. Catalysts consisting of compounds of bismuth or of copper may be added to the acid. This method may be utilized also for the separation of propylene and higher olefins from ethylene. Apgar[35] suggested treating a gas containing unsaturated hydrocarbons (propylene and butylene) with 70 to 90 per cent sulphuric acid under 100 to 150 pounds pressure at 21° to 27° C. After treatment with the acid, the immiscible oils are separated, and the alcohols recovered from the acid extract by hydrolysis and distillation.

The Société Anonyme d'Explosifs et de Produits Chimiques[36] separated cracking gases by liquefaction into fractions consisting of (1) pentanes and amylenes and (2) butanes and butylenes. Propylene and ethylene remaining in the residual gases are treated with cold sulphuric acid in which the propylene is absorbed, the ethylene remaining undissolved. Hydrolysis of the acid products followed by distillation yields isopropyl alcohol. Higher secondary and tertiary alcohols may be obtained by treating the liquid olefin fractions in a similar manner.

The process of Curme and Reid[37] for the production of isopropyl alcohol calls for the absorption of propylene in concentrated sulphuric or phosphoric acids at a temperature of —10° to 0° C., the temperature rising to 15° to 20° C. toward the end of the absorption. The product, containing as much as 80 per cent of diisopropyl sulphate, is hydrolyzed by emulsifying with water below 40° C. and the alcohol recovered in the usual manner.

Merley[38] described an interesting process for the production of alcohols from olefins. He sought to produce alcohols in a very pure state by eliminating the evil-smelling polymers principally by hydrolyzing the acid solution with four volumes of water and then dissolving the polymers in alcohols, particularly those having more than five carbon atoms. These higher alcohols are either formed during hydrolysis of the acid sulphates of the corresponding olefins originally present, or they are added during the operation.

Merley treated the gaseous olefins in a reaction chamber countercurrently with sulphuric acid. The absorption mixture then enters a second reaction chamber where liquid olefins are introduced, the reaction temperature being kept between

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[33] *Przemysl Chem.*, 1929, **13**, 208; *Chem. Abs.*, 1930, **24**, 1963. *Cf.* Holzman, *Allgem. Oel u. Fett-Ztg.*, 1931, **28**, 245; *Chem. Abs.*, 1932, **26**, 1107.

[34] I. G. Farbenindustrie A.-G., British Patent 324,897, 1928; *Brit. Chem. Abs.* **B**, 1930, 408. *Cf.* Suida, U. S. Patent 1,836,135, Dec. 15, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 994.

[35] U. S. Patent 1,846,666, Feb. 23, 1932; assigned to Sinclair Refining Co.; *Brit. Chem. Abs. B*, 1933, 11; *Chem. Abs.*, 1932, **26**, 2467.

[36] British Patent 251,652, 1927; *Chem. Abs.*, 1927, **21**, 1546.

[37] U. S. Patent 1,695,249, Dec. 11, 1928; assigned to Carbide and Carbon Chemical Corp.; *Chem. Abs.*, 1929, **23**, 609. *Cf.* Deanesly, British Patent 363,028, 1930; *Chem. Abs.*, 1933, **27**, 1421; Canadian Patent 310,439, 1931; *Chem. Abs.*, 1931, **25**, 3014; French Patent 704,876, 1930; *Chem. Abs.*, 1931, **25**, 4557; French Patent 718,943, 1931; *Chem. Abs.*, 1932, **26**, 3261; all patents assigned to Bataafsche Petroleum Maatschappij.

[38] U. S. Patent 1,809,788, June 9, 1931; assigned to Doherty Research Co.; *Chem. Abs.*, 1931, **25**, 4283.

0° and 5° C. The ester mixture is withdrawn to the acid settling tank where the hydrocarbons separate. From there the sulphuric ester mixture passes to the *drowning tank* where it is diluted with water, generally four volumes of water to one volume of the ester mixture, and cooled at the same time to prevent any rise in temperature. At this stage a large quantity of polymers separates and is decanted. The mixture is next conducted to a lead-lined hydrolysis tank, to which is attached a reflux condenser. Here, a heating appliance raises the temperature of the diluted mixture and hydrolysis occurs with the formation of alcohols. During heating and hydrolysis the temperature is kept low enough so that alcohol vapors are condensed by the reflux condenser. At the same time some of the polymer material, which had not previously separated, dissolves in the heavy alcohols having more than five carbon atoms. As stated above, if these alcohols are not formed from the olefins originally present they may be added in sufficient quantity before or after the dilution with water in order to dissolve the polymers and thus separate them from the other alcohols. Completion of hydrolysis is indicated when the surface layer temporarily changes in color from brown to green, which usually occurs after four hours of heating. The heating is immediately stopped and the resulting mixture of alcohols, water and acid quickly cooled. After cooling an additional quantity of the alcoholic solution of polymers rises to the surface and is withdrawn. The mixture of diluted acid and alcohol is then distilled in a lead-lined still and the following fractions are separated:

(1) Up to 80° C., consisting chiefly of ketones and some isopropyl alcohol.
(2) From 80° to 82° C., principally crude isopropyl alcohol of specific gravity 0.8166 to 0.8200.
(3) From 82° to 86° C., principally isopropyl alcohol together with some butyl alcohol, the mixture having a specific gravity of 0.82 to 0.848.
(4) From 86° to 88° C., crude butyl alcohol of specific gravity 0.848 to 0.863.
(5) From 88° to 100° C., containing the higher alcohols.

These fractions are further treated in the usual manner to obtain the various alcohols in a pure state.

A description of a method for the conversion of the olefins present in the gaseous and low-boiling products from cracking petroleum distillates in the vapor phase at about 610° to 620° C., into various secondary and tertiary alcohols has been given by Davis and Murray.[39] These olefins are first separated into several fractions, each of which is then further treated separately. It was determined by Davis and Murray that such olefins may be arranged in the order of increasing reactivity toward sulphuric and other polybasic acids [39a] shown in Table 82.

The initial separation of the olefins is effected as follows: The gases are first desulphurized and washed with cooled gas oil to dissolve the butylenes and higher olefins. The gas escaping from the scrubbers contains ethylene and propylene together with hydrogen and saturated hydrocarbons. The gas oil from the scrubbers passes into a still and on heating discharges its dissolved butylenes and amylenes (mixed with some paraffin hydrocarbons). By adjusting the temperature and pressure the amylenes are condensed and the butylenes pass on in gaseous form. This treatment results in the separation of the olefins from one another

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[39] British Patent 248,375, 1926; *Brit. Chem. Abs.* B, 1927, 403. U. S. Patents 1,790,517 and 1,790,523, Jan. 27, 1931. French Patent 614,023, 1926. All patents assigned to Petroleum Chemical Corp. See also Little, *J.S.C.I.*, 1929, 48, 202T.

[39a] Ormandy and Craven (*J. Inst. Pet. Tech.*, 1931, 17, 185; *Chem. Abs.*, 1931, 25, 2841; see Chapter 50) also observed that with acid concentrations of 81 to 92.8 per cent. olefins of high molecular weight were more resistant to sulphuric acid than those of low molecular weight. This was not true with higher concentrations of acid, however.

TABLE 82.—*Olefins Arranged in Order of Reactivity Toward Sulphuric Acid.*

Olefin	Boiling Point ° C.	State
Ethylene	— 103	Gas
Propylene	— 48.5	Gas
Pentene-1	39–40	Liquid
Pentene-2	36 (741 mm.)	Liquid
Butene-1	— 5	Gas, or in solution
Butene-2	1	Gas, or in solution
Isopropylethylene	21.1	Liquid
Unsymmetrical methylethylethylene	31–33	Liquid
Trimethylethylene	37–42	Liquid
Isobutylene	— 6	Gas, or in solution

into the following fractions, each of which also contains paraffin hydrocarbons and certain highly unsaturated substances:

(1) The gaseous fractions containing ethylene and propylene.
(2) The butylene fraction containing isobutylene, butylene-1 and butylene-2.
(3) The residue of the condensate which may contain each of the five isomeric amylenes and varying amounts of hexenes and higher olefins.

The ethylene-propylene fraction [i.e., fraction (1)] is first scrubbed with 80 to 84 per cent sulphuric acid to remove the highly reactive hydrocarbons, after which the propylene is absorbed in 95 to 100 per cent sulphuric acid at a temperature below 30° C., leaving the ethylene virtually unattacked. Isopropyl alcohol is then obtained in the usual way by hydrolysis and distillation.[40] Fractions (2) and (3) will be referred to again in Chapter 16 in connection with the production of the higher secondary and tertiary alcohols.

The Bataafsche Petroleum Maatschappij[41] suggested the use of certain catalysts for the absorption of ethylene and its homologues in sulphuric acid. These catalysts, among which may be mentioned potassium ferrocyanide and ferricyanide and other complex cyanides such as sulphoferricyanic acid, sodium nitroprusside, sodium ferrocarbonyl-pentacyanide, are said to minimize polymerization reactions. The absorption of butene-1, for example, is said to be effected by heating 90 grams of the butene with 400 grams of 70 per cent sulphuric acid and 10 grams of potassium ferrocyanide for several hours in an autoclave. The yield of butyl alcohol is 80 per cent. Butyl acetate can be prepared directly by heating glacial acetic acid with a similar mixture for 8 hours at 80° C. in an autoclave. Propylene can also be absorbed to the extent of 90 per cent in a liquid prepared by passing carbon monoxide or nitric oxide through a suspension of cuprous oxide (5 grams) in 90 per cent sulphuric acid (100 cc.).[41a] The isopropyl alcohol resulting on hydrolysis can be dehydrated with anhydrous potassium carbonate, calcium oxide, calcium chloride, or better, copper sulphate.[41b]

The direct esterification of propylene by a mixture of an organic acid and sulphuric acid was described by Woolcock.[42] Equal volumes of 99.5 per cent sulphuric acid and glacial acetic acid are treated with propylene at 40° C. until no more gas is absorbed. On diluting with water isopropyl acetate separates and from the diluted acid layer isopropyl alcohol can be recovered. Of the propylene absorbed 53 per cent appeared as isopropyl alcohol and 27 per cent as isopropyl acetate, while in a comparative experiment, using 99 per cent sulphuric acid alone, the yield of isopropyl alcohol was only 5 per cent, because of polymerization. In another example, oil gas containing 28 per cent propylene, 30 per cent ethylene and the remainder hydrogen and paraffin hydrocarbons was passed into a mixture of equal volumes of 99.5 per cent sulphuric acid and glacial acetic acid at a temperature of 40° C. The exit gas contained only 5 per cent propylene, and isopropyl alcohol and isopropyl acetate were recovered as before from the acid mixture.

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[40] For more specific information regarding this process and the method of operation the original references should be consulted: Davis, U. S. Patent 1,844,208, Feb. 9, 1932, and Davis and Murray, U. S. Patent 1,844,210, Feb. 9, 1932; both assigned to Petroleum Chemical Corp. Additional information concerning the process of the Petroleum Chemical Corp. is given in the following U. S. Patents: Davis, 1,790,519 and 1,790,520, Jan. 27, 1931; Davis and Harford, 1,790,521, Jan. 27, 1931; Davis and Murray, 1,790,517; 1,790,518; 1,790,522; Jan. 27, 1931.

[41] British Patent 323,748, 1930; *Brit. Chem. Abs.* **B**, 1930, 359. Also Dutch Patent 25,123, 1931; *Chem. Abs.*, 1932, **26**, 1939. French Patent 40,932, 1931; *Chem. Abs.*, 1933, **27**, 1359; addition to French Patent 677,822, 1929; *Chem. Abs.*, 1930, **24**, 3247; British Patent 381,723, 1932; *Chem. Abs.*, 1933, **27**, 3943. *Cf.* Chapter 13.

[41a] Bataafsche Petroleum Maatschappij, French Patent 695,707, 1930; *Chem. Abs.*, 1931, **25**, 2733; British Patent 336,633, 1930; *Chem. Abs.*, 1932, **26**, 5574.

[41b] Bataafsche Petroleum Maatschappij, French Patent 744,119, 1933; *Chem. Abs.*, 1933, **27**, 3943; French Patent 749,119, 1933; *Chem. Abs.*, 1933, **27**, 3943.

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[42] British Patent 334,228, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1930, 1058.

Chapter 15

Properties and Uses of Isopropyl Alcohol and Its Derivatives

Isopropyl alcohol has been produced in commercial quantities since about 1919, first by the Melco Chemical Co. and then by Standard Oil Co. of New Jersey, from the propylene of cracking gas. Since 1932 it has been manufactured by the Standard Alcohol Co., operating the Ellis process and including certain improvements of Davis and others. The industrial manufacture of this synthetic organic chemical is the direct result of the scientific exploration of petroleum as a chemical raw material. Although limited quantities of isopropyl alcohol have been manufactured in Europe by the hydrogenation of acetone, the production of this substance from the propylene of petroleum cracking has greatly reduced its cost and opened up a wide field of utility for both the alcohol and its many derivatives.

The production of isopropyl alcohol from the propylene of cracking gas amounted to about 37,500 gallons in 1922. In 1931, the production increased to about 1,500,000 gallons. It is now available in tank car lots at a price which makes it an economical solvent possessing advantages of great industrial significance.

The crude alcohol, resulting from the distillation of the dilute acid liquor, consists of isopropyl alcohol mixed with much water and small amounts of propyl ether, olefins and hydrocarbons. The crude alcohol stock may be purified by treating with alkaline calcium hypochlorite, alkaline potassium permanganate, silica gel or absorbent charcoal, followed by dehydrating with solid caustic soda, and finally fractionating. Usually, distillation of the aqueous alcohol is carried out to yield a constant-boiling mixture containing 91 per cent isopropyl alcohol and 9 per cent water. This azeotropic mixture is much more readily dehydrated than the corresponding ethyl alcohol azeotrope; a short digestion with an excess of dry solid caustic soda, followed by distillation, is sufficient to yield an anhydrous alcohol boiling at 82.4° C.[1]

The purification and deodorization of isopropyl alcohol is effected, according to Mann,[2] by the use of chlorine and decolorizing carbon. Agitation of the alcohol with a mixture of calcium hypochlorite and hydrochloric acid is suggested by Hudson[3] for the same purpose. Another process of purifying alcohols derived from olefins, proposed by Buc,[4] consists in agitating the alcohol with a highly refined petroleum distillate having an initial boiling point of 299° to 304° C., stratifying, separating and repeating the process six to eight times. The alcohol is then distilled. A method for extracting the polymers present in the crude alcohol or dilute acid liquor by a water-insoluble straight-chain mineral oil fraction [of which the initial boiling point is not less than 204° C. (400° F.)] has been described by Merley.[5]

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[1] Grant and Johns, *Amer. J. Pharm.*, 1922, 94, 418.

[2] U. S. Patent 1,502,149, July 22, 1924; *Chem. Abs.*, 1924, 18, 2901; assigned to Standard Oil Development Co.

[3] U. S. Patent 1,657,505, Jan. 31, 1928; *Brit. Chem. Abs.* B, 1928, 255; assigned to Standard Oil Development Co.

[4] U. S. Patent 1,712,475, May 7, 1929; *Brit. Chem. Abs.* B, 1929, 886; assigned to Standard Oil Development Co. In a later process for purifying alcohols, Buc (U. S. Patent 1,911,798, May 30, 1933) eliminates tertiary alcohols and analogous impurities with an acid of high boiling point.

Isham[6] employed benzenesulphonic acid for the separation of alcohols, such as those formed from mixed olefins, and dissolved polymers. The polymers are difficultly soluble in benzenesulphonic acid which readily extracts the alcohols. Lyons[7] distilled the crude alcohol with sufficient water to throw the hydrocarbon impurities out of solution in the alcohol. The low-boiling impurities are first distilled from the diluted liquid, and these are followed by a fraction of practically pure alcohol which can be collected separately.

PROPERTIES OF ISOPROPYL ALCOHOL

Pure isopropyl alcohol is a colorless liquid with a somewhat bitter taste and characteristic, though not unpleasant, alcoholic odor. It is miscible in all proportions with water but may be salted out of solution by saturating with sodium chloride or other salts.

The ternary systems, water-isopropyl alcohol-salts, have been studied quantitatively at 25° C. by Ginnings and Chen[8] for ten inorganic salts and qualitatively for a large number of others. Of all the salts investigated, potassium carbonate and potassium fluoride exhibited the greatest salting-out effect. These investigators further reported that isopropyl alcohol was easier to salt out than methyl or ethyl alcohol, but more difficult than either n-propyl alcohol or tertiary butyl alcohol.

The anhydrous alcohol may be prepared by treating the 91 per cent alcohol with 10 per cent of its weight of flake sodium hydroxide, withdrawing the aqueous layer formed, again treating with a small proportion of sodium hydroxide, decanting the alcohol layer, and distilling.[9] The alcohol so produced can be mixed with eight volumes of carbon disulphide, xylene, or petroleum ether without showing any trace of turbidity.

The addition of dry sodium chloride to dilute alcohol results in the formation of two liquid layers. The lower layer is an aqueous solution of sodium chloride, while the upper layer is 87 per cent isopropyl alcohol containing about 2 to 3 per cent sodium chloride. Distillation of the upper layer yields isopropyl alcohol of practically the same composition as the 91 per cent azeotropic mixture.

The boiling point of the anhydrous alcohol at atmospheric pressure is given variously[10] by a number of observers but the figure 82.4° C. may be taken as most reliable. Several workers have recorded specific gravities, all at 15° C./15° C., for anhydrous isopropyl alcohol with more or less variance as follows:

Observer	d_{15}^{15}
Thorpe[11]	0.7903
Doroshewski[12]	0.7898
Young[13]	0.7899
Lebo[14]	0.7902

[5] U. S. Patent 1,713,346, May 14, 1929; *Chem. Abs.*, 1929, **23**, 3341; *Brit. Chem. Abs.* **B**, 1929, 887; assigned to Doherty Research Co.

[6] U. S. Patent 1,732,894, Oct. 22, 1930; assigned to Doherty Research Co.; *Chem. Abs.*, 1930, **24**, 127.

[7] U. S. Patent 1,854,801, April 19, 1932; assigned to Doherty Research Co.; *Chem. Abs.*, 1932, **26**, 3261.

[8] *J.A.C.S.*, 1931, **53**, 3765. *Cf.* Frankforter and Temple, *J.A.C.S.*, 1915, **37**, 2697.

[9] Gilson, *J.A.C.S.*, 1932, **54**, 1445.

[10] 82.27° C. Brunel, Crenshaw and Tobin, *J.A.C.S.*, 1921, **43**, 561; 82.44° C. (corr), Young and Fortey, *J.C.S.*, 1902, **81**, 735; 82.28° C., Parks and Barton, *J.A.C.S.*, 1928, **50**, 24.

[11] *J.C.S.*, 1897, **71**, 920.

[12] *J. Russ. Phys.-Chem. Soc.*, 1909, **41**, 958; *Chem. Zentr.*, 1910, **1**, 157.

[13] *J.C.S.*, 1902, **81**, 728.

[14] *J.A.C.S.*, 1921, **43**, 1005.

Lebo obtained the value of d^{20}_4 as 0.7855 and found that the change in density per degree Centigrade was equal to 0.00080.

The vapor pressure of isopropyl alcohol of about 99.97 per cent purity was measured by Parks and Barton[15] with the results given in Table 83.

TABLE 83.—*Vapor Pressure Data for Isopropyl Alcohol.*

Temp. ° C.	Vapor Pressure Mm. Hg.	Temp. ° C.	Vapor Pressure Mm. Hg.
0.00	8.9	50.00	176.8
5.00	12.1	55.00	227.4
10.00	17.0	60.00	288.5
15.00	23.8	65.00	363.1
20.00	32.4	70.00	454.8
25.00	44.0	75.00	561.4
30.00	59.1	80.00	691.8
35.00	78.9	85.00	845.6
40.00	105.6	90.00	1020.7
45.00	136.8		

From the above data the molal heats of vaporization in calories were calculated to be 10,620 at 25° C., 10,490 at 50° C., and 9,600 at 82.28° C., and the molal entropy of vaporization is 33.8 calories per °C. at 38.7° C. The most reliable value of the heat of vaporization at 82.2° C. is 161.0 ± 1.5 calories per gram.[16]

Solid isopropyl alcohol melts at 184.67° K. (—88.46° C.) and the heat of fusion is 1284 calories per mole (21.4 calories per gram).[17]

According to Richardson and Sutton,[18] isopropyl alcohol has a flash point of 12° C. and a lower explosive limit, in air at 25° C., of 2.5 per cent by volume. Its auto-ignition temperature in air varies from about 457° C. in pyrex glass to 649° C., 634° C. and 638° C. in the presence of copper, steel, and chromium, respectively.[19]

The specific gravity (d^{20}_4) of isopropyl alcohol-water mixtures are given by Lebo[20] in Table 84.

TABLE 84.—*Specific Gravity of Isopropyl Alcohol-Water Mixtures.*

Alcohol by Weight Per Cent	d^{20}_4	Alcohol by Weight Per Cent	d^{20}_4
100.00	0.78556	53.07	0.89868
90.35	0.80866	43.02	0.92418
85.09	0.82282	33.17	0.94590
74.35	0.84828	21.39	0.96847
65.22	0.87003	9.58	0.98293

Young[21] found that the boiling point of the azeotropic mixture of isopropyl alcohol and water is 80.37° C., and it consists of 87.90 per cent of weight of alcohol. Mixtures containing more alcohol than this azeotropic mixture, on boiling, evolve a vapor richer in alcohol than the liquid, and those with a lower alcohol content give off, on boiling, a vapor poorer in alcohol than the liquid, the composition of the vapor tending to approach that of the constant-boiling mixture. Lebo investigated the boiling points of various isopropyl alcohol-water mixtures and found that the azeotrope has a boiling point of 80.4° C., a composition of 87.7 per cent alcohol by weight (or 91.1 per cent by volume) and a density (d^{20}_4) of 0.8158.

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[15] *J.A.C.S.*, 1928, **50**, 24.

[16] Parks and Nelson, *J. Phys. Chem.*, 1928, **32**, 61; *cf.* Brown, *J.C.S.*, 1903, **83**, 991; Matthews, *J.A.C.S.*, 1926, **48**, 562.

[17] Kelley, *J.A.C.S.*, 1929, **51**, 1145.

[18] *Ind. Eng. Chem.*, 1928, **20**, 187.

[19] Thompson, *Ind. Eng. Chem.*, 1929, **21**, 134.

[20] *Loc. cit.*

[21] *J.C.S.*, 1902, **81**, 728.

The critical temperature of isopropyl alcohol is 234.9° C., according to Pawlewsky.[22]

Isopropyl alcohol contains one hydrogen atom replaceable by metals to form isopropoxides and double compounds of this alcohol and calcium chloride and other inorganic salts are known. In chemical properties, isopropyl alcohol is a typical secondary alcohol yielding well-defined esters and ethers and being oxidized readily to acetone, the corresponding ketone.

USES OF ISOPROPYL ALCOHOL

Isopropyl alcohol is finding increasing application in industry and the arts, notably as a solvent, dehydrating agent, and preservative, in the preparation of medicinal extracts, in the manufacture of perfumes,[23] cosmetics, astringents,[24] shampoos,[25] and theater sprays, and as a resin solvent. Smith and Eoff [25a] suggest its use in flavoring extracts. Briefly, it is being used more and more as a substitute for ethyl alcohol, mainly because isopropyl alcohol is not subject to trade restrictions, as is ethyl alcohol. Isopropyl alcohol, since it is not taxed and is readily available, can be sold at a lower price than even tax-free ethyl alcohol, hence it is in a position to compete with ethyl alcohol for every use.

PHARMACOLOGY OF ISOPROPYL ALCOHOL

Some doubts have been raised from time to time as to whether the substitution of isopropyl for ethyl alcohol, particularly in perfumery and in the manufacture of cosmetics and mouth washes, is entirely free from objections from the point of view of public health. The following summarizes the principal results of pharmacological and toxicological investigations of isopropyl alcohol to date.

Macht [26] found that when injected intravenously into cats, isopropyl alcohol is twice as toxic as ethyl alcohol, four-fifths as toxic as normal propyl alcohol, and one-fourth as toxic as benzyl alcohol. This relative order of toxicity was substantiated by comparative experiments on the action of various alcohols on the isolated hearts of frogs, and on isolated plain muscle. When rats were exposed to air saturated with the vapor of various alcohols, methyl alcohol killed them in one or two days, whereas several days' exposure to the vapors of either ethyl or isopropyl alcohols produced no apparent injury. Furthermore, no subsequent blindness or defects of vision resulted from the inhalation of isopropyl alcohol vapor.

According to experiments of Burton-Opitz [27] the application of isopropyl alcohol to wounds in concentrations up to 50 per cent resulted in healing, apparently by normal granulation. Isopropyl was found to possess healing properties

[22] *Ber.*, 1882, 15, 3035; for heat of combustion see Zoubow, *J. Russ. Phys.-Chem. Soc.*, 1898, 30, 926.

[23] Ellis, U. S. Patent 1,582,912, May 4, 1926.

[24] Nolan and Ellis, U. S. Patent 1,891,440, Dec. 20, 1932.

[25] A "dry" (*i.e.*, water-free) shampoo of the isopropyl alcohol type has been on the market for many years under the name "Vapon" (see Ellis, U. S. Patents 1,700,035 and 1,700,036, Jan. 22, 1929; Hevdt, U. S. Patent 1,723,169, Aug. 6, 1929).

[25a] U. S. Patent 1,384,680, July 12, 1921; *Chem. Abs.*, 1921, 15, 3696.

[26] *J. Pharmacol. and Experim. Therapeutics*, 1920, 16, 1.

[27] Unpublished communication, quoted by Grant and Johns, *Amer. J. Pharm.*, 1922, 94, 418; *Chem. Abs.*, 1922, 16, 2944.

similar to those of ethyl alcohol, so far as these could be tested in dogs. When injected in small quantities and in concentrations of 10 to 100 per cent into the jugular vein and conjunctiva, the effect of isopropyl alcohol was approximately the same as that of ethyl alcohol.

Grant and Johns [28] reported that the use of isopropyl alcohol in lotions, liniments, antiseptic solutions for the throat, and in cleansing liquids, produced no noticeable injurious effects even after prolonged use. One of these investigators repeatedly took sponge baths from head to foot in 50 per cent isopropyl alcohol without injury.

An important detailed study of the physiological effects of isopropyl alcohol on rabbits, guinea pigs, dogs, cats, monkeys, and persons, by Fuller,[29] showed that when taken into the system in strength capable of being ingested without local discomfort, the animal economy is capable of absorbing this alcohol in reasonable amounts without toxic results. A form of intoxication is apparent, especially in the early part of the test, but a tolerance is quickly established and thereafter the outward appearance of intoxication differs in no respect from that induced by ethyl alcohol.

According to the observations of Munch and Schwartze,[30] the toxicity and the narcotic action of the alcohols of a homologous series increases with the molecular weight. A similar conclusion was also reached by Rost and Braun,[31] who found, however, that normal propyl alcohol is more active than isopropyl alcohol. It appears from the work of Kemal [32] that when isopropyl alcohol is administered to man it is excreted partly as acetone in the urine and in the breath; the amount of acetone excreted is greatly increased by drinking large amounts of water.

Bijlsma [33] critically examined the pharmacology of isopropyl alcohol with special reference to the question of its substitution for ethyl alcohol in cosmetics and mouth washes. Both alcohols have qualitatively the same effect on man and animals but quantitatively isopropyl is 2.4 times stronger than ethyl alcohol in the same molar concentration. The effect of drops in the eyes was the same for both alcohols. Local and general toxic effects were similar, the latter being quantitatively somewhat greater with isopropyl alcohol. Bijlsma concluded that the use of isopropyl alcohol in mouth washes and for external application need cause no concern.

In addition to the above, various opinions have been expressed regarding the use of isopropyl alcohol in the manufacture of cosmetics and toilet preparations. This alcohol exerts a definite disinfecting and preserving action and it has been used with success in the preservation of anatomical specimens.[34] Westermann [34a] found that the disinfecting value of aliphatic alcohols increases with their molecular weights. Boruttau [35] stated that there is no objection to the incorporation of isopropyl alcohol in cosmetics and toilet preparations,[36] and asserted that it can be safely used as a preservative in foods.[37]

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[28] *Amer. J. Pharm.*, 1922, **94**, 418; *Chem. Abs.*, 1922, **16**, 2944; Grant, *Amer. Perfumer*, 1921, **16**, 334; *Chem. Abs.*, 1922, **16**, 312.

[29] *J. Lab. Clin. Med.*, 1926, **12**, 326; *Chem. Abs.*, 1928, **22**, 2994.

[30] *J. Lab. Clin. Med.*, 1925, **10**, 985; *Chem. Abs.*, 1926, **20**, 1851.

[31] *Arb. Reichsgesundh.*, 1926, **57**, 580; *Chem. Abs.*, 1927, **21**, 2738.

[32] *Biochem. Z.*, 1927, **187**, 461; *Brit. Chem. Abs.* **A**, 1927, 990.

[33] *Arch. intern. Pharmacodynamie*, 1928, **34**, 204; *Physiol. Abs.*, **13**, 475; *Chem. Abs.*, 1929, **23**, 3741.

[34] Pope, *Science*, 1928, **68**, 487.

[34a] *Z. Hyg.*, 1933, **115**, 154; *Brit. Chem. Abs.* **B**, 1933, 654.

[35] *D. Med. Wschr.*, 1921, **47**, 747; *Chem. Zeit.*, Rep., 1921, **45** (154), 344; *Amer. Perfumer*, 1926, 262.

[36] See also, Löffl, *Seifensieder-Ztg.*, 1921, **48**, 542; *Chem. Abs.*, 1921, **15**, 3364. Fuller, *Chem. Met. Eng.*, 1923, **29**, 538.

[37] *Werteljahr. Ger. Med.*, 1919, **58**, 1; *Physiol. Abs.*, 1920, **5**, 48; *Chem. Abs.*, 1921, **15**, 273.

The Federal Board of Health of the German Republic on May 18, 1926, submitted (to the Minister of the Interior) the following opinion[88] regarding the use of isopropyl alcohol in medicines, cosmetics, foods, and other preparations. "According to the relatively meager toxicological researches on isopropyl alcohols, it can only be stated that in animal experiments, it possesses a higher narcotic effect than does ethyl alcohol. Since experiments regarding the effect of this higher alcohol on human beings and its fate in the animal and human body are scarcely available, it is impossible to decide whether or not the use of isopropyl alcohol instead of ethyl alcohol should be permitted. Even if it should be found that isopropyl alcohol is not more harmful to human beings than is ethyl alcohol—which is contrary to results of animal experiments—the introduction of this alcohol which is pharmacologically more active and certainly not less harmful than ethyl alcohol, should be opposed for the protection of public health." This Board consequently forbade the use of isopropyl alcohol in medicines and foodstuffs but failed to discover any well-founded objections from a sanitary standpoint against its use in the preparation of odorants, perfumes and the usual cosmetic preparations.

Later, in a session held on March 22, 1929, the Federal Board of Health of the German Republic adopted the following view regarding the use of isopropyl alcohol.[89] "Isopropyl alcohol offers no advantage over ethyl alcohol, either physiologically or pharmacologically, which can be advanced as reason for its use instead of ethyl alcohol. From the sanitary point of view, however, no objections can be raised against its use for perfumes, odorants, cosmetics, such as mouth and tooth washes, nail polishes, brilliantines, hair washes, bay rum and massage preparations—except French brandy, and as hand disinfectant. Isopropyl alcohol must, however, be excluded from general use in medicines, including French brandy, for internal as well as external use, and also in foodstuffs."

To summarize, it may definitely be concluded that the substitution of isopropyl alcohol for ethyl alcohol in certain of its uses, particularly in preparations which are applied externally, is entirely free from objection.

SOLVENT PROPERTIES OF ISOPROPYL ALCOHOL

Isopropyl alcohol has proved superior to ethyl alcohol in solvent properties for some uses, though there is often a striking difference between the solvent powers of the 91 per cent isopropyl alcohol-water azeotrope and the anhydrous alcohol. Applications of this alcohol as a solvent include the following:[40]

(1) *In the manufacture of fine organic chemicals and synthetic materials, for extracting pure substances from mixtures or for extracting impurities from insoluble substances, and as a recrystallizing solvent.* Isopropyl alcohol may advantageously be used in the preparation or purification of benzoic acid, salicylic acid, β-naphthol, saccharin, acetanilide, benzaldehyde, salol, benzidine, creosote carbonate, veronal, benzonaphthol, various dyes, heliotropin, santonin, aloin, tannin, coumarin, saponins, hydroquinone, alkaloids generally, and others.

(2) *In the preparation of solid medicinal extracts, plant principles and oleoresins.* Although official preparations must be extracted by ethyl alcohol or acetone, as the case may be, there is a large field for the use of isopropyl alcohol for non-official products of this nature, for example, in proprietary remedies and

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[88] *Reichs-Gesundheitsblatt,* 1926, 1, 810.

[89] *Reichs-Gesundheitsblatt,* 1929, 4, 549.

[40] For a review of the applications of isopropyl alcohol see, Grant and Johns, *Amer. J. Pharm.*, 1922, 94, 418; Valli-Donau, *Rev. parfumerie,* 1924, 4, 288.

flavoring compounds.[41] For the manufacture of such products isopropyl has important advantages over denatured grain alcohol on account of its purity and, where its solvent power is comparable with that of ether or acetone, it may replace these solvents advantageously with reduced fire hazard and diminished losses by evaporation.

(3) *As a solvent for medicinal substances for external medication.* The use of isopropyl alcohol in external medications should obviate the necessity for using poisonous or offensive denatured alcohol, expensive medicated alcohol and the rather costly pure ethyl alcohol. It should also be of value in the compounding of liniments, collodions, alcoholic lotions and antiseptic varnishes for burns. Ellis[41a] described the topical use of isopropyl alcohol in such preparations as witch-hazel extract and perfumes and as a rubbing alcohol in place of ordinary ethyl alcohol. The results obtained by Brandrup[42] indicated that this alcohol could be used advantageously in preparation of extracts of belladonna and cinchona. Despite its somewhat unpleasant taste, isopropyl alcohol can be incorporated in certain types of antiseptics for oral and nasal use and its solutions may be used for medicating surgical dressings.

(4) *In cosmetics.* The application of isopropyl alcohol as a solvent medium for the manufacture of perfumes, toilet waters, bay rum, hair tonics, bandolines, brilliantines, shampoo liquid or jelly, liquid rouge, and all kinds of cosmetic lotions, as well as in theater sprays is extensive.[43]

In the preparation of certain perfumes and barbers' specialties the odor of isopropyl alcohol has severely limited its application. In order to modify the odor and make it resemble that of ethyl alcohol more closely, Isham[44] proposed a solvent consisting of isopropyl alcohol, acetaldehyde, and butyl acetate in the proportion of 5 gallons of the alcohol, 3 cc. of acetaldehyde, and 6 cc. of butyl acetate.

(5) *In the laboratory.* Isopropyl alcohol is a useful solvent in the laboratory and may be employed for making solutions of phenolphthalein, methyl-orange, phloroglucinol, dimethylglyoxime and picric acid, as well as for standard soap solutions for water testing. It may be used in solvent extractions from aqueous solutions or from petroleum ether solutions. Miscibility is prevented, in the first case, by the addition of salts or alkalies to the water layer, and in the latter instance by adding water to the alcohol. Isopropyl alcohol can be employed in the preparation of staining solutions for bacteriological and pathological work. Its value in dehydrating tissues and in the preservation of biological specimens is already established. A number of tests carried out by Pope[45] on the preservation of newts gave favorable results with isopropyl alcohol solutions (aqueous) in concentrations of 40 to 50 per cent. Isopropyl alcohol competes in price with ethyl alcohol without the restrictions of the latter and is without the irritating properties of formaldehyde.

In connection with the use of isopropyl alcohol in pharmaceutical laboratories, Schamelhout[46] reports that it may be substituted for ethyl alcohol in the determination of acid numbers and saponification values of fats,[47] oils, and balsams, and also in such tests as the detection of rhapontic in rhubarb.

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[41] Luly, U. S. Patent 1,648,314, Nov. 8, 1927, proposes to employ as a solvent for drugs a mixture of isopropyl alcohol, acetic acid and water.

[41a] U. S. Patent 1,582,912, May 4, 1926.

[42] *Apoth. Ztg.*, 1931, **46**, 173; *Chem. Abs.*, 1931, **25**, 3432.

[43] *Vide* Valli-Donau. *Rev. parfumerie*, 1924. **4**. 288; *Chem. Abs.*, 1925. **19**, 703.

[44] U. S. Patent 1,692,662, Nov. 20, 1928; assigned to Doherty Research Co.

[45] *Science*, 1928, **68**, 487.

[46] *J. Pharm. Belge*, 1927, **9**, 401; *Chem. Abs.*, 1928, **22**, 1211.

[47] For the solubility of some vegetable oils in isopropyl alcohol of different concentrations see Hashi, *J. Soc. Chem. Ind. (Japan)*, 1931, **34**, 104B; 105B, 224B, 226B; *Chem. Abs.*, 1931, **25**. 3504; *Brit. Chem. Abs.* **B**, 1931, 894.

(6) *In the cellulose nitrate and cellulose acetate industries.* Although isopropyl alcohol is not a solvent for cellulose esters it has distinct latent solvent properties. Blending this alcohol with an ester, for example, yields a solvent for cellulose nitrate. Thus, Clough and Johns [48] propose a mixture of 47.5 per cent isopropyl acetate and 52.5 per cent isopropyl alcohol (azeotropic mixture, boiling at 80.1° C.) as a solvent for cellulose nitrate in the production of varnishes and films.

Isopropyl alcohol may serve as a solvent for camphor or camphor substitutes, in the preparation of plastics, "dopes," lacquers, films, and collodion.

(7) *As a resin solvent.* Isopropyl alcohol is a solvent for sandarac, mastic resins, common rosin and "bush kauri," and is a useful partial solvent for elemi, copal, and dammar. Isopropyl alcohol alone is not a good solvent for shellac. However, by adding a sufficient amount of methyl alcohol to the isopropyl alcohol, the shellac can be dissolved satisfactorily. Hudson [49] suggested employing a solution of a spirit-soluble gum, such as shellac, in 2 to 2.3 times its weight of isopropyl alcohol, as a glazing material for candy.

(8) *Miscellaneous.* Other applications of isopropyl alcohol as a solvent are in the production of wood stains and special dyeing materials, in the extraction of glycerol from distillery residues, in varnish and paint removers, in liquid soaps,[50] in disinfectant and deodorant solutions and insecticides, in dry cleaning preparations and, when mixed with hydrocarbons such as gasoline, as a paint or varnish thinner, degreasing agent, and motor fuel.[51] It has been proposed also as a solvent for the extraction of sulphonated compounds formed during the acid treatment of petroleum oils which are to be used for medicinal purposes.[52] Robinson [53] used isopropyl alcohol of at least 80 per cent concentration to revivify the spent fuller's earth from petroleum oil filtration operations. The extraction of lubricating oil from an asphalt-base residuum with this alcohol has been recommended by Taveau.[54]

After the vapor-phase oxidation of petroleum oils and removal of the lower boiling fractions (up to 300° C.), oxidation products may be extracted from the residue with 90 per cent isopropyl alcohol.[55] Dilution of the alcohol layer with water causes the separation of bodies which it is reported may be used as plasticizers for lacquers.

OTHER APPLICATIONS OF ISOPROPYL ALCOHOL

Anhydrous isopropyl alcohol proves a useful dehydrating agent in chemical, biological and photographic work, and may be used for drying nitrocellulose, sugars, starches, proteins, gelatin, and animal and vegetable tissues, for dehydrating histological specimens, and for cleaning and drying photographic prints and films. It can readily be recovered in an anhydrous state.

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[48] U. S. Patent 1,485,071, Feb. 26, 1924; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1924, **18**, 1389.

[49] U. S. Patent 1,646,731, Oct. 25, 1927; *Chem. Abs.*, 1928, **22**, 286.

[50] Heydt (U. S. Patent 1,723,169, Aug. 6, 1929; assigned to Petroleum Derivatives Co.; *Chem. Abs.*, 1929, **23**, 4543) proposes as a detergent composition for use on fabrics, isopropyl alcohol containing small proportion of tertiary butyl alcohol and sufficient water to give the composition a slow evaporation rate. Zimmermann (British Patent 334,177, 1928; *Brit. Chem. Abs.* **B**, 1930, 1037) states that the addition of a small quantity of isopropyl alcohol to acid soaps facilitates the incorporation of large proportions of fat solvents, such as benzene or terpenes.

[51] Mann, U. S. Patent 1,811,552, June 23, 1931; *Chem. Abs.*, 1931, **25**, 5049; assigned to Standard Oil Development Co.

[52] Cobb, U. S. Patent 1,387,835, Aug. 16, 1921; Robinson, U. S. Patent 1,387,868, Aug. 16, 1921; *Chem. Abs.*, 1921, **15**, 4048.

[53] U. S. Patent 1,403,198, Jan. 10, 1922; *Chem. Abs.*, 1922, **16**, 1011.

[54] U. S. Patent 1,825,762, Oct. 6, 1931; assigned to The Texas Company; *Chem. Abs.*, 1932, **26**, 590. See also Bataafsche Petroleum Maatschappij, British Patent 380,954, 1930; *Chem. Abs.*, 1933, **27**, 2741.

[55] James, U. S. Patent 1,835,600, Dec. 8, 1931; *Brit. Chem. Abs.* **B**, 1932, 877.

This alcohol may also be employed as a precipitant for proteins and peptones, for pepsin, trypsin, pancreatin, rennin, papain and other enzymes, as well as for various gums, sugars, soluble starches, silver protein compounds, and glycerophosphates.

Isopropyl alcohol is finding important application as a "key denaturant" for ethyl alcohol in various formulas for specially denatured alcohol to be used in the manufacture of perfumes and barbers' requisites.[56] Other important and likely applications of this versatile material are as an antidote for phenol burns, as a filler for thermometers, thermostats, and compasses, and in the preparation of anti-freeze liquids for automobile radiators.

ISOPROPYL ALCOHOL AS A CHEMICAL INTERMEDIATE

The availability of large supplies of isopropyl alcohol has opened up a wide field of possibilities in the commercial production of its derivatives. Already many of the esters of this alcohol are finding application as solvents or in perfumery and confectionery. Isopropyl ether is also attracting attention. Acetone can readily be produced from isopropyl alcohol (see Chapter 18). The isopropyl group may be introduced into organic compounds by means of isopropyl alcohol, thus making possible the production of a multitude of comparatively rare substances, some of which (e.g., thymol) find important industrial applications. Isopropylaniline and its homologues have been suggested as intermediates for the manufacture of dyes.[57] The product obtained on condensing a mixture of benzoin and isopropyl alcohol with naphthalene-β-sulphonic acid in the presence of sulphuric acid is said to be a distributing agent for insoluble substances.[58]

DETECTION AND ESTIMATION OF ISOPROPYL ALCOHOL

Methods for the detection and determination of isopropyl alcohol generally depend upon the oxidation of this alcohol to acetone, which is then recognized by the well-known nitroprusside test or otherwise. Other methods which have been proposed depend upon the reactions of this alcohol with piperonal and mercuric sulphate.

Rae[59] has suggested the following procedure for detecting isopropyl alcohol in wines and other liquors: Into a 200 cc. flask, place 20 cc. of a 1 per cent aqueous solution of potassium dichromate, 1 cc. of concentrated sulphuric acid and 10 cc. of the sample to be tested. The contents of the flask are distilled over a small flame using a bent glass tube as a condenser, and about 3 cc. of distillate is collected. The distillate is now carefully poured onto the surface of a solution consisting of 2 cc. of a 5 per cent sodium nitroprusside solution mixed with an equal volume of ammonia solution (sp. gr. 0.880) in a test tube to which about 2 grams of ammonium chloride has been added. The test tube is then set aside for a few minutes. If acetone, produced by the oxidation of isopropyl alcohol, is present a purple ring will appear at the junction of the two liquids. Rectified spirit gives a negative test by this method although methylated spirit reacts positively because of the presence of traces of acetone in the original. The reaction is stated to be sensitive to 0.1 cc. of isopropyl alcohol. A somewhat similar method, described by Henville,[60] is also sensitive enough to detect the presence of 0.1 per cent of isopropyl alcohol in wines.

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[56] For use of isopropyl alcohol as a denaturant for ethyl alcohol, see Guinot, *Z. Unters. Lebensm.*, 1931, 62, 330; *Brit. Chem. Abs.* **B**, 1932, 42. In 1931 the U. S. Government, as well as several foreign governments, adopted isopropyl alcohol as a denaturant. The present U.S.C.D.5 formula contains 5 volumes of isopropyl alcohol to every 100 volumes of ethyl alcohol, and formulas C.D.5A and C.D.10 each contain 2½ volumes to every 100 volumes of ethyl alcohol. Isopropyl alcohol is also used in several special formulas.

[57] Buc, U. S. Patent 1,555,451, Sept. 29, 1925; assigned to Standard Oil Development Co. Isopropyl-p-aminophenol, from isopropyl chloride and p-aminophenol, may be used in the dyeing of furs or in photographic developers: Buc, U. S. Patent 1,555,452, Sept. 29, 1925; assigned to Standard Oil Development Co.

[58] Soc. anon. pour l'ind. chim. à Bâle, Swiss patent 130,420, 1927; *Chem. Abs.*, 1929, **23**, 3060; Swiss Patent 133,377, 1927; *Chem. Abs.*, 1930, **24**, 475; Swiss Patent 136,544, 1928; *Chem. Abs.*, 1930, **24**, 4363.

[59] *Pharm. J.*, 1926, **116**, 630; *Chem. Abs.*, 1926, **20**, 3665.

According to Noetzel[61] the presence of isopropyl alcohol in ethyl alcohol produces but little change in density and boiling point but appreciably raises its refractive index. The use of indices of refraction as criteria is impractical with wines on account of the disturbing influence of acids and esters. Oxidation to acetone gives the best method of detecting isopropyl alcohol and the process may be made quantitative by determining the acetone produced, e.g., by combination with hydroxylamine hydrochloride and subsequent titration of the free acid produced.

The detection of isopropyl alcohol in brandy by oxidation to acetone, which is then recognized by Griebels' microbeaker method using m-nitrophenylhydrazine, has been described by Weiss.[62] An excellent method of detecting isopropyl alcohol in spirits, tinctures, still wine and cosmetics is that of Reif[63] and depends upon the production of a red or reddish-brown color when a mixture of sulphuric acid, isopropyl alcohol and piperonal (or anisaldehyde) is warmed on the water-bath for a few moments. By this method it is claimed that 1 per cent of isopropyl alcohol can be detected without first destroying the aldehydes, terpenes, and acetals present in the mixture. It may also be extended to the detection of isobutyl alcohol.

The detection of isopropyl alcohol by the formation of a precipitate with mercuric sulphate, as proposed by Stainer and Lauwaet,[64] has been criticized by Matthes and Schütz[65] as not sufficiently specific since this reagent also yields precipitates with unsaturated hydrocarbons and tertiary alcohols.

Nearly all the available methods for the quantitative determination of isopropyl alcohol utilize its oxidation to acetone as the first step, after which the acetone is determined quantitatively by one of several methods. One of the best methods of determining the acetone produced is that of Bennett.[66] This consists in treating the acetone with hydroxylamine hydrochloride (with which acetone reacts yielding acetoxime and hydrochloric acid), followed by titration of the liberated acid with a standard alkaline solution. This method has been recommended by a number of workers, notably by Simmons,[67] who has tested its accuracy. Noetzel[68] gives the following method for the determination of isopropyl alcohol in wines or alcohol: The sample of wine or alcohol is diluted with water until 100 cc. contain not more than 5 cc. of isopropyl alcohol. Twenty-five cc. of this solution is mixed with 50 cc. of a potassium dichromate solution (98 grams per liter), 100 cc. of 50 per cent sulphuric acid is added, and the mixture cooled. After standing for 3 hours at room temperature the unchanged chromic acid is reduced by adding 100 cc. of 25 per cent ferrous sulphate solution and the mixture is steam distilled. Seventy-five cc. of the distillate is collected in a vessel containing 5 cc. of 10 per cent caustic soda solution and 10 cc. of water. This distillate is redistilled, about 50 cc. being collected in a receiver containing 2 grams of hydroxylamine hydrochloride in 20 cc. of water. After shaking the latter mixture for 1 hour, the free hydrochloric acid is titrated with 0.25*N* caustic soda solution using methyl-orange as an indicator. As a blank, the hydroxylamine hydrochloride solution is titrated in the same manner. The result of the blank experiment is deducted from that for the distillate, and the weight of isopropyl alcohol is given by multiplying this difference by the factor 0.015.

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[60] *Analyst*, 1928, **53**, 416; *Chem. Abs.*, 1928, **22**, 3864; *cf.* Rae, *Analyst*, 1928, **53**, 646.

[61] *Z. Unters. Lebensm.*, 1927, **53**, 388; *Chem. Abs.*, 1927, **21**, 3582.

[62] *Z. Unters. Lebensm.*, 1929, **57**, 45; *Brit. Chem. Abs.* **B**, 1929, 619.

[63] In spirits and tinctures:—*Z. Unters. Lebensm.*, 1928, **55**, 204; *Chem. Abs.*, 1928, **22**, 3490; *Arch. Pharm.*, 1928, **266**, 382; *Chem. Abs.*, 1928, **22**, 3488; in still wines:—*Z. Unters. Lebensm.*, 1928, **55**, 204; *Brit. Chem. Abs.* **B**, 1928, 686; in cosmetics:—*Z. Unters. Lebensm.*, 1929, **57**, 277; *Chem. Abs.*, 1929, **23**, 5542; *Brit. Chem. Abs.* **B**, 1929, 737. See also *Z. Unters. Lebensm.*, 1930, **60**, 243; *Chem. Abs.*, 1931, **25**, 2077.

[64] *J. pharm. Belg.*, 1928, **10**, 167; *Chem. Abs.*, 1929, **23**, 4165.

[65] *Pharm. Z.*, 1929, **74**, 44; *Chem. Abs.*, 1929, **23**, 1593.

[66] *Analyst*, 1922, **47**, 146; *Chem. Abs.*, 1922, **16**, 2094.

[67] *Perf. Ess. Oil Rec.*, 1927, **18**, 168; *Chem. Abs.*, 1927, **21**, 2635.

[68] *Z. Unters. Lebensm.*, 1927, **53**, 388; *Brit. Chem. Abs.* **B**, 1927, 668.

The method of Archibald and Beamer,[69] which is applicable to mixtures of isopropyl and ethyl alcohols, is based on the difference in solubility of sodium hydroxide in the two alcohols. The procedure consists in agitating 10 cc. of the alcoholic mixture with 20 cc. of 30 per cent sodium hydroxide solution, and keeping the mixture at 25° C. during agitation. One cc. of the alcohol layer is then withdrawn and titrated with 0.1*N* sulphuric acid solution. The volume of acid required is then referred directly to a special graph from which the percentage of 91 per cent isopropyl alcohol by volume can be read off. This method can be used when the proportion of isopropyl alcohol does not exceed 50 per cent, most accurate results being obtained with mixtures containing less than 20 per cent isopropyl alcohol. When more than 50 per cent of isopropyl alcohol is present, the original mixture must be diluted with a definite volume of ethyl alcohol and the isopropyl alcohol content of the diluted mixture determined.

When isopropyl alcohol is to be estimated in a mixture of acetone and this alcohol, the acetone content may be determined first by any known method. After oxidation of the isopropyl alcohol the acetone content is determined again, and the difference between the two values thus obtained represents the acetone produced from isopropyl alcohol. According to Cassar [70] the oxidation of isopropyl alcohol to acetone may be carried out quantitatively in the presence of the latter by using chromic acid. By using a definite volume of a chromic acid solution of known concentration and back-titrating the excess acid (with potassium iodide and sodium thiosulphate solution) the amount of isopropyl alcohol in the mixture may be determined in less than one hour. This method is of course applicable only when the alcohol is not mixed with other readily oxidizable materials.

Adams and Nicholls [71] have devised a rapid procedure for the detection and colorimetric determination of acetone, and thus of isopropyl alcohol. This is based on Penzoldt's method,[72] in which indigo is formed as a condensation product when sodium hydroxide is added to a mixture of o-nitrobenzaldehyde and acetone. To 10 cc. of a solution containing not more than 0.02 gram of acetone, add 1 cc. of 1 per cent solution of o-nitrobenzaldehyde in 50 per cent ethyl alcohol, mix, add 0.5 cc. of 30 per cent aqueous caustic soda and allow to stand for 15 minutes, avoiding strong daylight. The color produced is then compared with standards similarly treated. To detect isopropyl alcohol by this method the alcohol is first oxidized with bromine water and the acetone estimated. Five cc. of saturated bromine water is added to 10 cc. of a solution containing not more than 10 per cent by volume of alcohol, and the mixture allowed to stand 3 to 6 hours, or longer, in a cold place. The acetone produced is then determined colorimetrically as just described.

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[69] *Ind. Eng. Chem., Analyt. Ed.*, 1932, 4, 18.

[70] *Ind. Eng. Chem.*, 1927, 19, 1061; *Brit. Chem. Abs.* **A**, 1927, 1100.

[71] *Analyst*, 1929, 54, 2; *Brit. Chem. Abs.* **B**, 1929, 162; *Chem. Abs.*, 1929, 23, 1367.

[72] *Z. Anal. Chem.*, 1885, 24, 149.

DERIVATIVES OF ISOPROPYL ALCOHOL

The large scale production of isopropyl alcohol has made possible the preparation and study of a large number of derivatives of this alcohol, hitherto unknown or known only in relatively small amounts. Already some of these derivatives are finding important applications in industry while others are being investigated.

Isopropyl Ether. Of the derivatives of isopropyl alcohol, isopropyl ether is becoming important as an industrial solvent. It is a liquid with a sweet and somewhat camphoraceous odor, boiling point of 67.5° C., and specific gravity 0.7247 (20°/20° C.). It is made on a large scale by the dehydration of isopropyl alcohol by means of warm, moderately concentrated sulphuric acid, though other acids may also be used. Apparently the catalytic dehydration of isopropyl alcohol in contact with ordinary dehydrating oxide catalysts, such as alumina, at higher temperatures, leads almost exclusively to the formation of propylene.[73] Even when using sulphuric acid of less than 85 per cent concentration, much propylene is always produced simultaneously with the isopropyl ether. Thus Mann[74] prepared this ether by heating a mixture of isopropyl alcohol and dilute sulphuric acid of 70 to 85 per cent concentration to 100° to 125° C. and condensing the ether from the vapors evolved. The gaseous propylene, simultaneously formed, is absorbed in sulphuric acid and isopropyl alcohol recovered. For example, 75 per cent sulphuric acid is mixed with 1.25 to 1.5 times its volume of 90 per cent isopropyl alcohol and the mixture is distilled through a fractionating column, the temperature of the liquid mixture being maintained at 100° to 125° C., and the temperature at the top of the column at 45° to 65° C. The ether is carried over with the gaseous propylene and is condensed, while the propylene is absorbed in concentrated sulphuric acid at about 10° C., or lower, to yield isopropyl alcohol. The yield of ether is approximately 40 per cent of the theoretical.

In another process for the manufacture of aliphatic ethers, the alcohols are heated to temperatures as high as 300° C. under high pressures in the presence of dehydrating catalysts.[75] Thus on heating isopropyl alcohol in a closed vessel with aluminum sulphate for 4 hours at 210° to 215° C. under a pressure of 53 to 100 atmospheres, a yield of isopropyl ether amounting to 14 per cent of the theoretical was obtained. The process is also applicable to the production of other dialkyl ethers. Purification of isopropyl ether by 65 to 80 per cent sulphuric acid, followed by dilution with water, separation of the insoluble ether and distillation, has been described by Buc.[76]

Isopropyl ether has been suggested as a solvent[77] for animal, vegetable and mineral oils, and for certain waxes and resins. It may be employed also in the extraction of acetic acid, or other aliphatic acids, from aqueous solutions. Mixtures of this ether and ethyl acetate have been proposed for the same purpose.[78] Acetone containing 5 to 20 per cent of isopropyl ether can be used in the preparation of artificial silk of low luster.[79]

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[73] See, for example, Trautz and Winkler, *J. prakt. Chem.*, 1922, **104**, 44; *Chem. Abs.*, 1923, **17**, 722; Allardyce, *Trans. Roy. Soc. Can.*, 1927, (3) **21**, Sect. 3, 315; *Chem. Abs.*, 1928, **22**, 1521. Ormandy and Craven (*J.S.C.I.*, 1929, **48**, 291T) reported that isopropyl alcohol and phosphoric acid at 170°-175° C. yielded propylene, hydrocarbons which were largely polymerides of propylene, and saturated hydrocarbons, probably open-chain paraffins.

[74] U. S. Patent 1,482,804, Feb. 5, 1924; *Chem. Abs.*, 1924, **18**, 988.

[75] Bataafsche Petroleum Maatschappij, British Patent 332,756, 1929; *Brit. Chem. Abs.* **B**, 1930, 981.

[76] U. S. Patent 1,442,520, Jan. 16, 1923; *Chem. Abs.*, 1923, **17**, 1029.

[77] Fife and Reid, *Ind. Eng. Chem.*, 1930, **22**, 513.

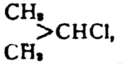
[78] E. B. Badger and Sons Co., British Patent 371,554, 1931; *Brit. Chem. Abs.* **B**, 1932, 792.

[79] Ruth-Aldo Co., Inc., British Patent 385,673, 1931; *Brit. Chem. Abs.* **B**, 1933, 187.

Apparently this ether cannot be successfully substituted for ethyl ether as a solvent in the Grignard reaction.[80] In the presence of isopropyl ether, the reaction between magnesium and the organic halide either does not take place, or else the yield of products is very much less than when ethyl ether is employed.

It has been shown by Clover[81] that this ether, like other simple ethers, slowly takes up oxygen when exposed to the air and sunlight. The products obtained from isopropyl ether are hydrogen peroxide, acetone and isopropyl alcohol; the intermediate substance is probably a peroxide of the type $(C_3H_7)_2O{\cdot}O_2$.

Acetals. Various acetals may be prepared by the action of isopropyl alcohol on the appropriate aldehyde in the presence of a catalyst such as hydrogen chloride, calcium chloride or ferric chloride.[82] Diisopropylacetal, $CH_3CH(OC_3H_7)_2$, is a colorless liquid of boiling point 125.5° to 126.5° C. and d_4^{25} 0.8128.[83]

Isopropyl Chloride. This substance,  $\begin{matrix}CH_3\\ \quad>CHCl\\ CH_3\end{matrix}$, is a pleasant-smelling, non-corrosive liquid of boiling point 36.5° C. and $d_4^{15.6}$ 0.866. It is an excellent solvent for fats and may replace carbon disulphide and petroleum ether to some extent in the fat extraction industry. It may also be used as a refrigerant in certain types of machines. Its application in large scale organic synthesis, though undoubtedly great, is still largely unexplored.[84] This halide may be made by the direct esterification of isopropyl alcohol with hydrochloric acid. Unlike tertiary alcohols, secondary alcohols, of which isopropyl alcohol is typical, do not immediately react with hydrochloric acid alone but readily combine in the presence of an excess of zinc chloride at 26° to 27° C. Primary alcohols do not react with hydrochloric acid under these conditions. This fact may be used to detect the presence of secondary and tertiary alcohols in the presence of a primary alcohol.[85] Norris and Taylor[86] reported that 60 to 82 per cent yields of isopropyl and other alkyl chlorides are obtained by refluxing a mixture of alcohol, concentrated hydrochloric acid, and an excess of zinc chloride.

According to McKee and Burke,[87] alkyl halides may be conveniently produced by passing a mixture of the alcohol and halogen acid in the vapor phase over a catalyst which consists of a solid salt of a bivalent metal, e.g., magnesium chloride, at a temperature of about 300° C.

The halides may be easily freed from polymers by boiling gently with concentrated sulphuric acid under a reflux condenser. The purified chloride is then separated from the mixture either by decantation or by distillation.[88]

The direct esterification of isopropyl alcohol with hydrobromic and hydriodic acids is much more readily effected than with hydrochloric acid.

DIISOPROPYL SULPHATE

Diisopropyl sulphate may be prepared, according to Ormandy and Craven,[88a] by the absorption of propylene in concentrated sulphuric acid at very low temperatures. It may also be obtained in 34 per cent yield by adding isopropyl alcohol slowly to a solution of sulphuryl chloride in carbon tetrachloride at 0° C., followed by washing with ice water and distillation *in vacuo*. The method was employed by Levaillant,[89] who gives the following physical constants for isopropyl sulphate: boiling point 78° to 80° C. at 3.7 mm., d_0^0 1.118, n_D^{17} 1.409. This sulphate may be prepared also by the action of sulphuryl chloride on sodium isopropylate,[90] both dissolved in ether, at temperatures of —10° to —15° C. Isopropyl sulphate should prove useful in introducing the isopropyl group into organic compounds just as methyl sulphate has proved a valuable methylating agent.

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[80] Rathmann and Leighty, *Trans. Illinois State Acad.*, 1931, 24, 312; *Brit. Chem. Abs.* A, 1932, 728.

[81] *J.A.C.S.*, 1924, 46, 419. The peroxide actually isolated by Clover showed an active oxygen content greater than that indicated by the formula $(C_3H_7)_2O{\cdot}O_2$. It was therefore suspected of being a mixture of this peroxide and a similar derivative of acetone.

[82] Adams and Adkins, *J.A.C.S.*, 1925, 47, 1358.

[83] Adkins and Broderick, *J.A.C.S.*, 1928, 50, 178.

[84] Grant and Johns, *Amer. J. Pharm.*, 1922 (June).

[85] Lucas, *J.A.C.S.*, 1930, 52, 802.

[86] *J.A.C.S.*, 1924, 46, 753.

[87] U. S. Patent 1,738,193, Dec. 3, 1929.

[88] Norris, U. S. Patent 1,825,814, Oct. 6, 1931; *Chem. Abs.*, 1932, 26, 480; assigned to Petroleum Chemical Corp.

[88a] *J.S.C.I.*, 1930, 49, 362T.

The sulphonation of isopropyl alcohol, mixed with high-boiling petroleum fractions, by chlorosulphonic acid at temperatures of about 35° C. yields substances which have been proposed as cleaning, emulsifying or wetting agents.[91]

Isopropyl Acetate. This is undoubtedly the most important of the esters of isopropyl alcohol from an industrial point of view. Ellis and co-workers proposed making this ester by the direct esterification of propylene with acetic acid using sulphuric acid as a catalyst,[92] or by absorbing propylene in sulphuric acid and then adding a salt of acetic acid, such as calcium acetate.[93] Isopropyl acetate is generally made, however, by the esterification of isopropyl alcohol with acetic acid in the presence of a condensing agent, such as sulphuric acid. An example of this esterification process follows:[94] Commercial isopropyl alcohol, containing 10 per cent of water and a little tertiary-butyl alcohol, is distilled with 100 to 200 per cent excess of glacial acetic acid and a catalyst, e.g., 0.2 to 0.3 per cent of concentrated sulphuric acid. The still-head temperature is maintained at 75.5° C. and the isopropyl acetate coming over is condensed and separated from the aqueous layer. Yields of 65 to 80 per cent are obtained before the concentration of acetic acid falls to 65 per cent, at which point the distillation is stopped.

When necessary, isopropyl acetate may be freed from the isopropyl alcohol by water-washing. Mann[95] has devised a process for purifying esters of this type which consists in treating the alcohol-ester mixture with water and a mineral oil distillate [of an initial boiling point of 163° C. (325° F.) or higher]. The alcohol is more soluble in the water than in the oil-ester layer so that separation ensues. The oil-ester layer is separated and distilled to yield the purified ester.

Isopropyl acetate is a colorless liquid of fragrant odor. The boiling point of this substance as formerly given (92° C.) is apparently incorrect, since Grant and Johns[96] report a value of 88.5° to 89.0° C., and Haggerty and Weiler,[97] from an accurate determination of the change of vapor pressure of this substance with temperature, found it to be 88.2° C. The vapor pressure is given by the expression:

$$\mathrm{Log}_{10}\, P = 14.2517 - 2.0972 \log_{10} T - \frac{2170.1}{T}.$$

Its density is 0.877 at 15.6° C.[96]

The technical product has a specific gravity of 0.865 to 0.900, a boiling range of 82° to 95° C. and an acidity of 0.02 per cent acetic acid. It is miscible with benzene to a clear solution in all proportions.[98]

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[89] *Compt. rend.*, 1929, **188**, 261. *Cf.* Ormandy and Craven, *J.S.C.I.*, 1930, **49**, 362T.

[90] Medvedev and Alexejeva, *Ber.*, 1932, **65**, 131.

[91] Lindner, British Patent 313,861, 1927; *Brit. Chem. Abs.* **B**, 1929, 708.

[92] U. S. Patent 1,365,052, Jan. 11, 1921.

[93] U. S. Patent 1,365,050, Jan. 11, 1921.

[94] Buc, U. S. Patent 1,808,155, June 2, 1931; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1931, **25**, 4285. See also British Patent 300,418, 1927; *Brit. Chem. Abs.* **B**, 1929, 315.

[95] U. S. Patent 1,541,430, June 9, 1925; *Chem. Abs.*, 1925, **19**, 2210.

[96] *Amer. J. Pharm.*, June 1922.

[97] *J.A.C.S.*, 1929, **51**, 1623.

Isopropyl acetate is a good solvent for cellulose nitrate and its evaporation rate, being about one-third that of ethyl acetate, is not rapid enough to cause water blush. Accordingly this ester is useful in pyroxylin lacquers. It is also a good solvent for ester gum, cumarone, elemi, sandarac, mastic, and kauri. It partly dissolves shellac, will not dissolve cellulose acetate or hard copals, and is miscible with hydrocarbons.[98a]

It forms a constant-boiling mixture with isopropyl alcohol (boiling point 80.1° C.) containing 47.5 per cent of ester and 52.5 per cent of alcohol. As previously noted, this mixture has been proposed as a solvent for cellulose nitrate.[99]

Other Isopropyl Esters. The isopropyl esters of organic acids are similar in properties to the corresponding esters of ethyl alcohol. The esters of formic, butyric, valeric, benzoic and salicylic acids have been prepared and may find application in the perfume and essence industry. Isopropyl formate (together with other esters of formic acid) in the vapor state has been found to be toxic to the rice weevil and to have no effect on the germination of wheat. It thus appears to be of value as a fumigant against various stored-products insects. Additions of 60 to 75 per cent by volume of carbon tetrachloride are recommended to free this and other formates of possible fire hazard when thus used.[100] Isopropyl chloroacetate has also been shown to possess a high toxicity and hence to be of value as a fumigant.[101]

Halogenation of Isopropyl Alcohol

The chlorination of isopropyl alcohol yields not only acetone and chlorinated acetones but also chloropropanes and other substances. According to Brochet [102] when isopropyl alcohol is treated with dry chlorine in the cold the product consists mainly of tetrachloroacetone (boiling point 183° C., d^{15}_{4} 1.624, and n^{18}_{D} 1.497). According to Buc [103] the chlorination of isopropyl alcohol to yield chlorinated acetones is best carried out below 70° C., while at higher temperatures the products are chlorinated propanes. Thus it is proposed to manufacture chloropropanes by passing chlorine into boiling isopropyl alcohol. As chlorination proceeds the boiling point of the mixture rises and in the later stages of the chlorination the reaction temperature is maintained at 85° C. The chlorinated product is a heavy liquid which settles out at the termination of the reaction. The products consist [104] mainly of 1,2- and 2,2-dichloropropanes, boiling point 97° to 98° C. and 69.7° C., respectively, and are non-flammable solvents.

Buc [105] has also reported a process for making pentachloroacetone by the chlorination of isopropyl alcohol. Isopropyl alcohol is chlorinated to a mixture of di- and trichloroacetones by treatment with chlorine at 35° to 70° C. (best at

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[98] Durrans, "Solvents," Chapman and Hall, London, 1930.

[98a] The increasing importance of isopropyl alcohol as a solvent is shown by an estimate of the 1933 consumption, which reveals that it comprised about 25 per cent of all the low-boiling acetates sold to the lacquer trade.

[99] Clough and Johns, U. S. Patent 1,485,071, Feb. 6, 1924; *Chem. Abs.*, 1924, **18**, 1389.

[100] Cotton and Roark, *Ind. Eng. Chem.*, 1928, **20**, 380.

[101] Roark and Cotton, *Ind. Eng. Chem.*, 1928, **20**, 512; for the vapor pressures of various alkyl chloroacetates see Nelson, *Ind. Eng. Chem.*, 1928, **20**, 1380.

[102] *Compt. rend.*, 1894, **119**, 1270; *Chem. Soc. Abs.*, 1895, **68** (1), 259.

[103] U. S. Patent 1,391,758, Sept. 27, 1921; assigned to Standard Oil Development Co.; *J.S.C.I.*, 1921, **40**, 827A.

[104] Grant and Johns, *loc. cit.*

[105] U. S. Patent 1,391,757, Sept. 27, 1921; assigned to Standard Oil Development Co.; *J.S.C.I.*, 1921, **40**, 827B; *Chem. Abs.*, 1922, **16**, 260.

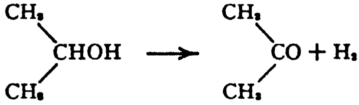
65° C.) under which conditions the formation of chlorinated hydrocarbons is minimized. The chloroacetone may be salted out of solution by inorganic salts. The mixed chloroacetones are further chlorinated in the presence of an excess of water at a temperature of 70° to 100° C. A substantially complete conversion of the lower chloroacetones into pentachloroacetone is effected in 48 to 60 hours.

Dippy, Watson and Yates [106] reported that the principal products of the reaction of bromine and isopropyl alcohol are isopropyl bromide and the unsymmetrical tetrabromoacetone. Along with these products are also obtained some monobromo-, 1,1-dibromo-, and 1,1,1-tribromoacetone.

CONVERSION OF ISOPROPYL ALCOHOL INTO ACETONE

Although acetone is now made very cheaply and economically by certain fermentation processes, isopropyl alcohol from petroleum is available in quantity as a source of this ketone.[107] On the other hand, there appears to be a tendency, especially in Europe where supplies of isopropyl alcohol are not readily available, to utilize acetone as a raw material for the production of isopropyl alcohol.

The conversion of isopropyl alcohol into acetone may be carried out either by catalytic dehydrogenation or by partial oxidation, both reactions resulting in a loss of hydrogen thus:



Where oxidation is employed, the hydrogen is, of course, removed as water. These processes are described more completely in Chapter 18.

SYNTHESES WITH ISOPROPYL ALCOHOL

One of the most important and promising reactions of isopropyl alcohol from an industrial standpoint is its condensation with various aromatic substances to yield isopropylated derivatives. In this reaction, which is brought about under the influence of a condensing agent such as sulphuric acid, the isopropyl alcohol probably functions as a source of nascent propylene, since olefins are known to condense with aromatic substances to yield alkylated products. In some cases, n-propyl alcohol, and even propylene itself, may be substituted for its isomer, another indication that propylene is an intermediate in the process.

This type of reaction may be illustrated by a process developed by the I. G. Farbenindustrie A.-G.[108] Nuclear-substituted arylalkylated or cycloalkylated compounds are obtained by treating either carbocyclic or heterocyclic hydrocarbons with the acid sulphuric esters of alcohols having three or more carbon atoms. For example, benzene is alkylated by mixing it with the acid sulphuric ester of isopropyl alcohol (from chlorosulphonic acid and isopropyl alcohol), adding sulphuric acid, and warming.

This type of synthesis has been extended to the preparation of mixed ethers.[109] To illustrate, isopropyl ter.-butyl ether is made by heating a mixture of isopropyl alcohol and ter.-butyl alcohol, in the presence of sulphuric acid, to temperatures of about 100° C.

Many of the isopropylated derivatives of aromatic hydrocarbons are wetting, emulsifying, and foam-producing materials. It has been proposed to add sulphonic acid salts of isopropylnaphthalene to acid fiber-treating baths such as are used in carbonization of woolen fabrics or in dyeing.[110] Aqueous solutions of sulphonic acids of polynuclear isopropylated aromatic hydrocarbons are said to be of aid in the hydrolysis of fats, oils and waxes.[111] Another application of these emulsifying agents is in the conversion of insoluble substances such as resins or dyes, into emulsions or suspensions. The insoluble substance is first dissolved in a liquid immiscible with water and the solution is emulsified in water with the aid of, e.g., isopropylnaphthalenesulphonic acid. Emulsions of dyes or lakes may be used for dyeing many classes of materials.[112]

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[106] *J.C.S.*, 1931, 2508; *Brit. Chem. Abs.* A, 1931, 1267.

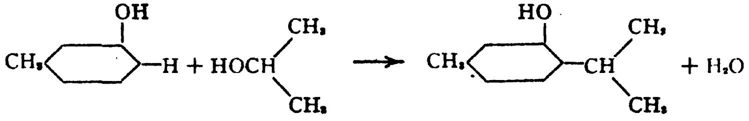
[107] Baldwin, *J.S.C.I.*, 1930, 49, 53T; *Ind. Eng. Chem., News Ed.*, 1930, 8 (2), 12.

[108] British Patent 267,132, 1926; *Chem. Abs.*, 1928, 22, 1164. French Patent 33,067, 1927; addition to French Patent 608,949; *Chem. Abs.*, 1929, 23, 1136.

[109] Bataafsche Petroleum Maatschappij, French Patent 739,266, 1932; *Chem. Abs.*, 1933, 27, 1890.

Production of Thymol

Isopropyl alcohol may be used as an isopropylating agent in the production of thymol. The starting materials are m-cresol and isopropyl alcohol (or propylene) and the reaction may be represented as follows:



Thymol

The condensing agent may be phosphoric acid,[113] but sulphuric acid is usually recommended. Thus, m-cresol is sulphonated to a mixture of di- and tri-sulphonic acids by treatment with oleum at 150° C. To this mixture is then added a solution of isopropyl alcohol in concentrated sulphuric acid and the whole is maintained at 90° C. for several hours. The product is then steam-distilled to yield thymol, the sulphonic acid groups being split off during the step.[114] Instead of isopropyl alcohol, n-propyl alcohol may be employed.[115] According to the Rheinische Kampfer Fabrik,[116] thymol may be produced by heating m-cresol with isopropyl (or n-propyl) alcohol in an autoclave at 350° C., in the presence of catalysts effecting the conversion into propylene. Water is distilled off and the heating is repeated after the addition of more alcohol. The yield of thymol is equivalent to 60 to 70 per cent of the unrecovered m-cresol. If propyl chloride is used as a source of propylene, zinc oxide or other acid absorbent is added.

Various syntheses from isopropyl alcohol, including a method for the production of thymol, have been described by Bert.[117]

Thymol is a crystalline solid (melting point, 51.5° C. and boiling point, 232° C.) and an important antiseptic. It is widely used in dentifrice and mouthwash preparations and forms a component of many ointments, soaps, and embrocations used in treating skin diseases.

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[110] Pott, U. S. Patent 1,686,836, Oct. 9, 1928; assigned to Chemische Fabrik Pott and Co.; *Chem. Abs.*, 1928, 22, 4835. *Cf.* Pospiech, British Patent 248,814, 1924; assigned to Chemische Fabrik Pott and Co.; *Chem. Abs.*, 1927, 21, 826.

[111] Schrauth, Canadian Patent 235,373, 1924.

[112] I. G. Farbenindustrie A.-G., British Patent 264,860, 1927; *Brit. Chem. Abs.* **B**, 1928, 648.

[113] Blagden, British Patent 200,151, 1922; assigned to Howards and Sons, Ltd.; *Chem. Abs.*, 1924, 18, 274.

[114] Blagden, British Patent 197,848, 1922; assigned to Howards and Sons; see also Badische Anilin- und Soda-Fabrik, British Patent 186,202, 1921; *J.S.C.I.*, 1922, 41, 879A; Günther, U. S. Patent 1,412,937, Apr. 18, 1922; Andrews, U. S. Patent 1,306,512, June 10, 1919; McKee, U. S. Patent 1,449,121, Mar. 20, 1923. For a criticism of the above patents see Schindelmeiser and Pam, *Chem. and Drug.*, 1923, 296.

[115] Badische Anilin- und Soda-Fabrik, German Patent 379,952, 1921; addition to German Patent 350,809; *J.S.C.I.*, 1924, 43, 403B.

[116] British Patent 312,907, 1929; addition to British Patent 293,753, 1928; *Brit. Chem. Abs.* **B**, 1930, 1017.

[117] *Bull. soc. chim.*, 1925, (4) 37, 1252; *Chem. Abs.*, 1926, 20, 1793.

Chapter 16

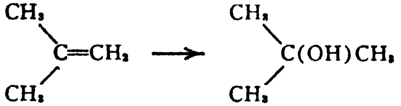
Reaction of Sulphuric Acid with Higher Homologues of Ethylene and Propylene. Production of Higher Secondary and Tertiary Alcohols

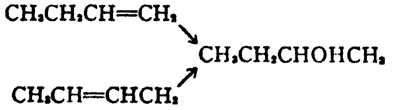
Esterification of the olefins of more than three carbon atoms with sulphuric acid is a more complicated reaction than that of propylene. The extent to which side reactions (polymerization and splitting of the polymers) proceeds depends very largely on the molecular structure of the olefin and on the experimental conditions, especially the acid concentration and temperature. The higher olefins react much more rapidly with sulphuric acid than either ethylene or propylene, so that it is possible to effect reaction by using acid of comparatively low concentrations. Fairly dilute acid is indeed usually essential for good yields of higher alcohols, since more concentrated acid causes considerable polymerization and it is impossible to obtain alcohols from some olefins even by using comparatively dilute acid on this account.

A résumé of the work on the reactions of individual olefins with sulphuric acid is given in this chapter. Industrial processes for the manufacture of the higher secondary and tertiary alcohols will be discussed together rather than as subdivisions under each individual olefin.

THE BUTENES

The tendency of olefins to form alkylsulphuric esters first increases with molecular weight attaining a maximum for the amylenes (pentenes) and hexenes and then declines.[1] The three butenes, particularly isobutene, show a marked affinity for sulphuric acid. Not only are alkylsulphuric acids formed but also (with more concentrated acid) considerable amounts of polymers. However, under certain conditions (namely at fairly low temperatures with sulphuric acid of sufficiently low concentrations) all the butylenes may be converted into the corresponding alkylsulphuric acids and subsequently hydrolyzed to alcohols. In this manner isobutene is convertible into tertiary butyl alcohol and the two other butylenes (butene-1 and -2), into secondary butyl alcohol.





$$CH_3CH_2CH{=}CH_2 \searrow \quad CH_3CH_2CHOHCH_3 \quad \nearrow CH_3CH{=}CHCH_3$$

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[1] Brooks and Humphrey, *J.A.C.S.*, 1918, 40, 822. See also Brooks, U. S. Patent 1,879,599, Sept. 27, 1932; assigned to Petroleum Chemical Corp.; *Chem. Abs.*, 1933, 27, 312.

Of the three butenes, isobutene is by far the most reactive toward sulphuric acid and other reagents. Butlerow[2] studied the reaction of sulphuric acid of different strengths with isobutene. Trimethyl carbinol was produced with a diluted acid containing 5 parts sulphuric acid and 1 part of water. With stronger acid, a water-insoluble oil was obtained. Investigations of the velocity of absorption of isobutylene in sulphuric acid and the formation of polymerized hydrocarbons were carried out by Berthelot.[3] Faworsky and Debout[4] used the reactivity of isobutene with diluted sulphuric acid as a means for separating this olefin from pseudobutylene (butene-2), the former being soluble in diluted sulphuric acid of approximately 17 per cent strength and the latter insoluble. Data on the proportions of the three butenes absorbed by sulphuric acid (in Hempel pipettes with definite periods of shaking) were given by Michael and Brunel.[5] Their results showed that in each experiment the rate of absorption of the butene was approximately proportional to the quantity undissolved. From the experimental results of Michael and Brunel, Davis[6] calculated a specific absorption coefficient, K, for each butene according to the equation

$$K = \frac{1}{t} \ln \frac{1}{1-x}$$

where t = the number of minutes the pipette was shaken, and x = the fraction of olefin absorbed in time t. Table 85 shows the values obtained.

TABLE 85.—*Absorption Coefficients, K, for the Butenes in Sulphuric Acid.*

Olefin	Conc. of H_2SO_4, Per Cent	Temp. ° C.	K
Isobutene	58.6	21–22	47×10^{-3}
Isobutene	58.6	28–29	105×10^{-3}
Butene-2	58.6	28–29	0.54×10^{-3}
Butene-2	76	29–30	10×10^{-3}
Butene-1	76	29–30	5×10^{-3}

On the basis of these figures Davis calculated that the relative rates of absorption of the three butenes in sulphuric acid are in the ratio of the following figures:

Isobutene	280–390
Butene-2	2
Butene-1	1

Later Davis and Schuler[7] reported some important data on the relative rates of absorption of the gaseous olefins by sulphuric acid at 25° C., in which it was shown that:

(1) Propylene and butene-1 dissolve at about the same rates in sulphuric acid of any concentration.

(2) The ratio of the absorption of butene-2 to butene-1 is remarkably constant, being 1.7 to 2.6 for 70 per cent to 87 per cent acids.

(3) The values for isobutene varied in a puzzling manner, but on the average it dissolved about 10 to 80 times as rapidly as butene-2.

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[2] *Z. Chem. Pharm.*, 1870, 236. *Cf.* Bataafsche Petroleum Maatschappij, British Patent 360,331, 1931; *Brit. Chem. Abs.* **B**, 1932, 221.

[3] *Compt. rend.*, 1894, 118, 1009.

[4] *J. prakt. Chem.*, 1890, **42** (2), 152.

[5] *Amer. Chem. J.*, 1909, **41**, 118.

[6] *J.A.C.S.*, 1928, **50**, 2780.

[7] *J.A.C.S.*, 1930, **52**, 721.

ISOBUTENE

The conditions necessary for the conversion of isobutene into tertiary butyl alcohol with sulphuric acid were first elucidated by Butlerow.[8] Isobutene in the liquid state was allowed to react with 2 volumes of 50 per cent sulphuric acid in a sealed tube at room temperature until solution had taken place. The acid was then diluted, carefully neutralized, and distilled. The tertiary alcohol was salted out of the distillate with potassium carbonate. The polymerizing action of even relatively dilute acid on isobutene was also noticed by Butlerow, who found that when a solution of this olefin in 50 per cent sulphuric acid was warmed to 100° C. the dipolymer (di-isobutene) was produced. On introducing isobutene into a cooled mixture of 5 parts of concentrated sulphuric acid and 1 part of water, Butlerow[9] observed the formation of tri-isobutene. According to Nef[10] butene is quantitatively converted into polymers by concentrated sulphuric acid.

The hydration of isobutene to tertiary butyl alcohol may apparently be effected by comparatively dilute organic acids. Miklaschewsky[11] obtained this alcohol by warming isobutene with a 5 to 10 per cent aqueous solution of oxalic acid at 35° to 40° C.

Michael and Brunel showed that isobutene is rapidly and completely dissolved by sulphuric acid of 63 per cent strength at 17° C., but these workers did not differentiate between the formation of alcohols and alkylsulphuric esters, and reactions of polymerization and rearrangement.

A method for the conversion of isobutyl alcohol into tertiary butyl alcohol through the intermediate formation of isobutene was described by Read and Prisley.[12] Isobutyl alcohol is dehydrated at 500° to 520° C. in the presence of alumina on pumice to yield, mainly, isobutene. The isobutene is then cooled and bubbled through three absorption vessels containing kerosene (cooled to about 0° C.) until the volume of the kerosene had increased by about one-half. An equal volume of cooled 50 per cent sulphuric acid is added to this solution and the mixture shaken vigorously for several hours. It was necessary to keep the reaction mixture cooled to about 0° C., but toward the end of the agitation the temperature was permitted to rise to that of the room. The mixture is allowed to stand to separate the kerosene layer, and the acid layer is neutralized by pouring it, drop by drop, into a well-cooled aqueous solution of sodium hydroxide. The alkaline solution is distilled and the tertiary alcohol salted out of the distillate in the usual way. Under these conditions the other butenes present in the gas are unchanged. It should be noted that great care is required in recovering the tertiary alcohol from the acid solution because of the ease with which this alcohol is dehydrated to isobutene. As dehydration takes place readily in the presence of dilute acids, neutralization of the acid before distilling is essential.

BUTENE-1 AND -2

The conversion of butene-2 into secondary butyl alcohol was investigated by King.[13] The liquefied olefin was agitated under its own pressure in contact with acids of varying strength. At higher acid concentrations polymerization took place, but with 78 per cent acid the formation of polymers was very slight. Acids below this strength yielded normal reactions. In one case an absorption of nearly 21 per cent in excess of the butene theoretically required to give butylsulphuric acid was observed. This suggested that the latter is capable of directly hydrating butene-2. Distillation with water produced a good yield of secondary butyl alcohol. The results of the experiments in relation to acid concentration, absorbed butene in grams per 50 cc. of acid, and time are shown in Table 86.

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[8] *Ann.*, 1876, **180**, 246; 1877, **189**, 48.
[9] *Ber.*, 1879, **12**, 1482.
[10] *Ann.*, 1901, **318**, 26; *Chem. Soc. Abs.*, 1901, **80** (1), 626.
[11] *J. Russ. Phys.-Chem. Soc.*, 1890, (1), 495; *Ber.*, 1891, **24**, 269 Ref.
[12] *J.A.C.S.*, 1924, **46**, 1512.
[13] *J.C.S.*, 1919, **115**, 1404.

TABLE 86.—*Absorption of Butene-2 by Sulphuric Acid.*

Acid Conc. (per cent)	Butene-2 in Grams	Time
100	17	——
84	21	5 minutes
78	23	20 minutes
76	22	40 minutes
75.3	22	1 hour
72.5	19	1–6 hours
70	24	5 hours
64.8	10	8 hours
50	22	Little effect after 15 hours

With 100 per cent acid the absorption accompanied by the formation of polymers was complete in a few seconds. With 84 per cent acid, alcohol was the main product, although considerable polymerization occurred. With 78 per cent acid, a trace of an oil with a turpentine-like odor was observed on dilution with water. This was imperceptible with lower concentrations. With higher concentrations a considerable rise in temperature was noted, but with 75 per cent acid the temperature did not reach 40° C. Dilution of the acid solution before distillation with an equal weight of water was adopted as giving the best yields (about 89 per cent) of alcohol. From secondary butyl alcohol, methyl ethyl ketone was obtained by dehydrogenating over reduced copper at approximately 290° C.

The Weizmann and Legg[14] process for the manufacture of secondary butyl alcohol consists in mixing liquid normal butene with cooled 75 per cent acid and subsequently diluting and distilling the acid solution.

A somewhat similar method is described by Newman.[15] The butene (possibly a mixture of isomers made by dehydrating n-butanol at 360° C.) is compressed and treated with 60 per cent sulphuric acid. The reaction is highly exothermic and some dibutyl ether is formed. After the absorption, the acid liquor is diluted, distilled and the secondary alcohol recovered from the distillate. This alcohol can be dehydrogenated catalytically to yield methylethyl ketone. The efficiency of this latter operation was stated to be 90 per cent.

The profound polymerizing effect (accompanied also by rearrangement and splitting of the polymers) of 98 per cent sulphuric acid at 25° C. on the mixture of butenes, resulting from the dehydration of n- and iso-butyl alcohols at 350° to 400° C., was observed by Ormandy and Craven.[16] They were unable to isolate alcohols or alkylsulphuric acids but found the reaction products to consist of a mixture of paraffin and highly unsaturated hydrocarbons.

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[14] U. S. Patent 1,408,320, Feb. 28, 1922; *Chem. Abs.*, 1922, 16, 1593.

[15] *Can. Chem. J.*, 1920, 4, 47; *Chem. Abs.*, 1920, 14, 1120. See also Toussaint, *J. Phar. Belg.*, 1921, 3, 221; *Chem. Zentr.*, 1921, 4, 123.

[16] *J.S.C.I.*, 1928, 47, 317T. Whitmore and Wrenn (*J.A.C.S.*, 1931, 53, 3136) determined the isomers in the "diisobutylene" obtained on treating commercial tertiary butyl alcohol with diluted sulphuric acid (see Chatper 26).

THE PENTENES (AMYLENES)

The five isomeric pentenes have been the subjects of much investigation but it is only in the last few years that their reactions with sulphuric acid have been made clear. Much of the earlier work is contradictory on account of the fact that mixtures of isomers (obtained in various ways) were investigated and because the isolation of pure individual pentenes is often a matter of extreme difficulty. Etard[17] investigated commercial amylene and found it to contain four isomers. Two, ethylmethylethylene and trimethylethylene, are soluble in sulphuric acid diluted with half its volume of water (about 66.6 per cent acid). Two, isopropylethylene and "normal amylene", are insoluble in this acid.

The experiments of the earlier investigators, however, pointed to the conclusion that although amyl alcohols could be produced by the action of sulphuric acid on amylenes, polymerization always played an important part. Thus, Berthelot noted that small quantities of amylene hydrate were formed by the action of sulphuric acid upon "amylene". Erlenmeyer observed only the formation of a dimer, diamylene, under the influence of this reagent. His failure to obtain an alcohol[18] from "amylene" by the sulphuric acid reaction even led him to the conclusion that this hydrocarbon apparently did not belong to the same series as propylene and hexylene, which could be transformed into the alcohols by this method.

Flavitsky[19] conducted a slow stream of carbon dioxide charged with amylene vapor into a mixture of 2 parts of sulphuric acid and 1 part of water. A portion of the amylene was converted into diamylene but the rest dissolved, and, on the addition of water, an alcohol separated from this solution. The alcohol boiled between 100° and 108° C. and was thought to consist in part of dimethylethylcarbinol (tertiary amyl alcohol). Later Osipoff[20] treated commercial amylene with sulphuric acid of various concentrations. With acid of 1.67 sp. gr. (at 20° C.) he obtained an alcohol, believed to be identical with dimethylethylcarbinol. The product was a colorless liquid, smelling like camphor and bitter almond oil, boiling at 96° to 97° C. and solidifying at —30° C. With acid of 1.545 sp. gr. (at 20° C.) the resulting alcohol had a boiling point of 102°-103° C. and did not solidify at —30° C. (probably methylisopropylcarbinol).

The formation of polymers by the action of sulphuric acid of various strengths on "amylene" (usually a mixture of isomers) was noted by a number of observers. Thus, Butlerow[21] found that when amylene, prepared from tertiary amyl alcohol, was mixed with sulphuric acid (2 volumes of concentrated acid to 1 volume of water), diamylene separated. Wischnegradsky[22] stated that amylene, of boiling point 35° C., when shaken with sulphuric acid, sp. gr. 1.64, dissolves after a time and on standing two days gives diamylene. Amylene prepared by the action of zinc chloride on fermentation alcohol was only partially soluble in acid diluted with one-half its volume of water.[23] Wischnegradsky[24] also noted that isopropylethylene did not dissolve at 0° C. in acid diluted with one-half of its volume of water. He claimed[23] to have obtained large amounts of fusel oil by the action of cold concentrated acid on "amylene", the alcohol being isolated by diluting the acid layer with water, thus precipitating an oil consisting, in part, of an amyl alcohol. It must be remembered that isopropylethylene is the most stable of the amylenes, and is therefore an important constituent of "amylene". Under certain conditions, however, it isomerizes to trimethylethylene.[25] Schneider[26] described the preparation of diamylene from amylene (boiling point 35° to 37° C.) by mixing it with twice its volume of sulphuric acid (2 volumes of concentrated acid to 1 volume of water).

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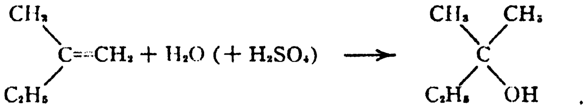
[17] *Compt. rend.*, 1878, 86, 488.
[18] *Z. Chem. Pharm.*, 1865, 362; see also Berthelot, *Compt. rend.*, 1894, 118, 1009.
[19] *Ann.*, 1873, 165, 157; *Ber.*, 1872, 5, 479.
[20] *Ber.*, 1875, 8, 1240.
[21] *Ann.*, 1878, 189, 75.
[22] *Ber.*, 1875, 8, 434; see also *Ber.*, 1877, 10, 81.
[23] *Ann.*, 1878, 190, 328.
[24] *Ann.*, 1878, 190, 354.

One of the first systematic studies of the relative reactivities of the lower olefins was conducted by Michael and Brunel,[27] who observed that tetramethylethylene reacts readily and completely with 77 per cent acid at ordinary temperatures but not so readily as trimethylethylene. Unsymmetrical methylethylethylene dissolved more readily in 66 per cent acid than did isopropylethylene. One of the amylenes, namely unsymmetrical methylethylethylene, prepared by the dehydration of dimethylethylcarbinol, was found by Brooks and Humphrey[28] to be completely dissolved in 2 volumes of 85 per cent sulphuric acid in a few minutes at 10° C. A 45 per cent yield of the tertiary alcohol was liberated from the solution by diluting with ice water, and no formation of polymers was observed. Apparently the hydration of this methylethylethylene proceeds according to the reaction:



The relative rates of absorption of trimethylethylene and isopropylethylene, compared with those of the lower olefins, in sulphuric acid were examined by Davis and Schuler.[29] They reported that trimethylethylene vapor was absorbed three to four times faster than gaseous isobutene by 80 per cent acid and 1.3 times faster by 70 per cent acid. Isopropylethylene was absorbed slowly by 70 per cent acid at a rate comparable with that of propylene.

A comprehensive work on the action of sulphuric acid on the individual pentenes is that of Norris and Joubert.[30] With the possible exception of pentene-1, all the amylenes were prepared in a pure state and the relative reactivities tested.[31] Equimolecular quantities of olefin and sulphuric acid of various concentrations were introduced into tubes, sealed, and shaken. The progress of the reaction was observed by the changes in the volumes of the contents of the tubes at various time intervals. Amylenes having two radicals linked to an unsaturated carbon atom (e.g., trimethylethylene and unsymmetrical methylethylethylene) reacted much more rapidly with acids of lower concentration than did their isomers. Thus, at room temperature trimethylethylene and unsymmetrical methylethylethylene dissolved in an equimolecular quantity of 60 per cent acid in approximately one-twentieth of the time required to effect solution of either pentene-1 or pentene-2. Norris and Joubert arranged the amylenes in the following order based on the decreasing rate of reaction with sulphuric acid: (1) trimethylethylene, (2) unsymmetrical methylethylethylene, (3) symmetrical methylethylethylene (pentene-2), (4) pentene-1, and (5) isopropylethylene. Whereas the difference in the reactivities of trimethylethylene and unsymmetrical methylethylethylene was slight (trimethylethylene dissolving slightly more rapidly), these hydrocarbons were much more reactive than pentene-2 and pentene-1. Isopropylethylene was affected only by acids of polymerizing strength, and it was impossible to obtain an alcohol from this olefin.[32]

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[25] Ipatiev, *Ber.*, 1903, **36**, 2004; Senderens, *Compt. rend.*, 1920, **171**, 916.

[26] *Ann.*, 1871, **157**, 207.

[27] *Amer. Chem. J.*, 1909, **41**, 118.

[28] *J.A.C.S.*, 1918, **40**, 822.

[29] *J.A.C.S.*, 1930, **52**, 721.

[30] *J.A.C.S.*, 1927, **49**, 873.

[31] The pentene-1, prepared by Norris and Joubert from allyl bromide and ethyl bromide, boiled at 39°-41° C. After their work had been completed Kirrmann (*Bull. soc. chim.*, 1926, **39**, 988), using a similar method of preparation, obtained pentene-1 having a boiling point of 30.5° to 31° C. As pointed out by Norris and Joubert the chief difficulty in this method of preparation is the separation of ethyl bromide, ether and pentene-1, as the boiling points of these substances do not differ greatly. Later Bourguel (*Bull. soc. chim.*, 1927, **41**, 1475) prepared pentene-1 by the catalytic hydrogenation of the corresponding acetylene derivative, and obtained a product boiling at 32.5° C. Following this, Dykstra, Lewis and Boord (*J.A.C.S.*, 1930, **52**, 3396) prepared pentene-1 from its dibromide and found the boiling point to be 29°-31° C. Apparently pure pentene-1 boils about 30°-31° C. and not 39°-41° C. as earlier investigators believed.

To make alcohols from the pentenes (isopropylethylene excepted) it is essential to use acid of the lowest concentration necessary to effect solution at ordinary temperatures. Increasing the concentration of the acid invariably results in the production of polymers. With trimethylethylene slight polymerization was noted using 57 per cent acid, but polymerization was complete in two days in contact with 70 per cent acid. Unsymmetrical methylethylethylene gave similar results. With pentene-1 and pentene-2, much stronger acid (84 to 86 per cent) was needed to give noticeable polymerization. Isopropylethylene was the only pentene which did not dissolve in sulphuric acid, although 75 per cent acid produced complete polymerization in six days. The experiments of Norris and Joubert further showed that relatively small quantities of concentrated acid are capable of effecting almost complete polymerization. When 10 moles of trimethylethylene were shaken with 1 mole of concentrated sulphuric acid, immediate polymerization occurred, the product consisting mainly of the dimer. Using similar proportions of olefin and acid, isopropylethylene yielded with concentrated acid a product boiling above 200° C. (no dimer) and with 75 per cent acid after 7 days, a material consisting almost entirely of the dimer.

These investigators also gave some information regarding the conditions necessary for the production of alcohols from several of the pentenes. Thus, it was found that the addition of ammonium sulphate to a solution of olefins in sulphuric acid (the ammonium sulphate reacting with sulphuric acid to give ammonium acid sulphate) produced interesting results. With hydrocarbons yielding tertiary amyl alcohol, the latter was immediately precipitated in the free state, but from solutions of pentene-1 and pentene-2, the alcohol did not separate until water had been added to permit hydrolysis. On the basis of this observation it was believed that the formation of alcohol was the result of the direct addition of water to an olefin under the catalytic influence of sulphuric acid. In the case of secondary alcohols, subsequent combination of the alcohols (so formed) with sulphuric acid to yield alkylsulphuric acid must be assumed. It was noted that about five equivalents of trimethylethylene could be converted into tertiary amyl alcohol by shaking successive amounts of the olefin with 46 per cent sulphuric acid. The free alcohol was obtained by extraction with ether or by the addition of ammonium sulphate.

Pentene-1 and pentene-2 can be readily converted into alcohol, according to Norris and Joubert, by shaking the hydrocarbon with an equal volume of 84 per cent sulphuric acid, diluting the solution with 8 volumes of water, and distilling the mixture. The portion of the alcohol dissolved in the aqueous distillate is precipitated by adding salt or sodium hydroxide. The time required for solution of the olefin in the acid can be shortened by using 86 per cent acid, provided the reaction mixture is kept cool.

Direct hydration of trimethylethylene to tertiary amyl alcohol in the presence of a 5 to 10 per cent aqueous solution of oxalic acid at 100° C. for a few days was observed by Miklaschewsky.[33]

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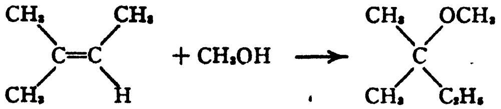
[32] Michael and Zeidler (*Ann.*, 1911, 385, 252) found, however, that with 10 volumes of either 38 or 47 per cent acid, solution of unsymmetrical methylethylethylene took place in approximately seven-tenths of the time required by trimethylethylene.

The direct combination of methyl alcohol and trimethylethylene,[34] in the presence of sulphuric acid as a condensing agent, at 95° C. results in a 50 per cent yield of a methyl amyl ether, boiling point 86° C. The reaction may probably be represented as follows:



According to Norris and Davis,[35] the butenes and pentenes may be divided on the basis of (a) their reactivity with sulphuric acid, (b) the alcohols produced, and (c) their tendency to form high-boiling oils into the following three main groups:

Group 1. Members of this group dissolve readily in 60 to 70 per cent sulphuric acid, yielding tertiary alcohols, and are easily polymerized by hot dilute acid or by concentrated acid in the cold. They are (1) isobutene, (2) trimethylethylene, and (3) unsymmetrical methylethylethylene.

Group 2. Almost insoluble in sulphuric of any concentration. Yield no secondary alcohol and only a trace of tertiary alcohol and are polymerized more slowly than the members of Group 1. The only member of this group is isopropylethylene.

Group 3. Members of this group dissolve in moderately concentrated acid (75 to 80 per cent) and the products, on immediate hydrolysis, yield secondary alcohols. They are much more resistant to polymerization than the members of Groups 1 and 2. This group includes butene-2, butene-1, pentene-2, and pentene-1.

The above classification corresponds closely with results obtained in the large-scale production of alcohols in which a complex mixture of olefins is split up into these groups by absorption in sulphuric acid of graded concentrations.

The Hexenes

Erlenmeyer and Wanklyn[36] were among the first to investigate the reaction of sulphuric acid with hexene. By varying the concentrations of the acid used, different results were obtained. Thus, 99.3 per cent acid yielded polyhexenes, and the same acid plus one volume of water furnished the β-hexylalcohol. Experiments on the sulphuric acid absorption of butylethylene were carried out by Brochet,[37] who found that this olefin was insoluble in a mixture of three parts of sulphuric acid and one part of water. Le Bel,[38] however, studying the pyrolytic decomposition of the oils derived from bituminous substances (from the mines of Schwabwiller, Pechelbronn and Lobsanne), observed the transformation of hexene into isohexyl alcohol by absorption in sulphuric acid followed by the addition of water and distillation.

Brooks and Humphrey[39] examined the action of sulphuric acid on the straight-chain olefin hydrocarbons of more than five carbon atoms. They concluded that the tendency of aliphatic hydrocarbons to form alkylsulphuric esters and alcohols increases with increasing molecular weight, reaching a maximum with the pentenes and hexenes. Reference has already been made to the observation of Brooks and Humphrey that on pouring a solution (obtained by dissolving simple olefins such as the hexenes in 85 per cent sulphuric acid at temperatures not above 15° C.) into iced water the free alcohol corresponding to a proportion of the olefin dissolved is immediately precipitated, while ordinarily about 30 per cent to 40 per cent of the hydrocarbon remains in the diluted solution in combination as the alkylsulphuric ester. On treating a mixture of hexenes with 100 per cent acid, no alcohols were formed. Larger yields of alcohol were obtained using 85 per cent than 94 per cent acid. It was concluded that the water initially present in the reaction mixture, and not the water in the subsequently diluted solution, enters into the reaction.

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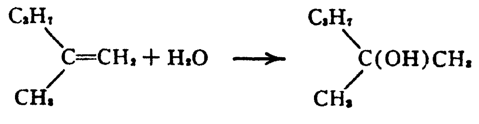
[33] *J. Russ. Phys. Chem. Soc.*, 1890, **22**, 495; *Ber.*, 1891, **24**, Ref. 269.
[34] Reychler, *Bull. soc. chim. Belg.*, 1907, **21**, 71; *Chem. Zentr.*, 1907, **1**, 1125.
[35] *J.S.C.I.*, 1929, **48**, 70T.
[36] *Ann.*, 1865, **135**, 141; see also *J. der Chemie*, 1863, 520.
[37] *Compt. rend.*, 1892, **114**, 601.
[38] *Bull. soc. chim.*, 1872, **18** (2), 146.
[39] *J.A.C.S.*, 1918, **40**, 822.

Pursuing these investigations, Brooks and Humphrey studied the action of sulphuric acid on a number of hexenes and mixtures of hexenes. They treated 200 grams of a mixture of hexenes (produced by the action of alkali on mixed monochlorohexanes) with 1.25 moles of sulphuric acid (d 1.84), the temperature being allowed to rise to 40° C., and obtained 117 grams of a mixture of hydrocarbons (unchanged hexenes, dimers, and higher polymers). The acid layer on dilution yielded 58 grams of an oil (probably a mixture of hexyl alcohols), and the aqueous layer was proved to contain hexylsulphuric acids. A summary of the work on hexene-1, 2-methylpentene-1, and tetramethylethylene, is given below.

Fifty-two grams of pure hexene-1 were added to 100 cc. of 85 per cent acid at 15° C. during a period of about 20 minutes. Complete solution to a clear, viscous, amber-colored solution took place. The solution was poured into 4 volumes of water and cracked ice. Separation into two layers occurred, the bulky supernatant layer consisting of hexylsulphuric acid and free alcohol. On adding 6 volumes of cold water to this supernatant liquor the hexylsulphuric acid passed into solution and the free alcohol layer remained. From this layer 28.0 grams of the free alcohol, of d_{20}^{20} 0.823, was recovered. This secondary hexyl alcohol distilled at 134° to 138° C. and on acetylation yielded an acetate boiling at 154° to 158° C. The hexyl alcohol prepared in this way probably has the constitution, $CH_3CH_2CH_2CH_2CHOHCH_3$. No polymers were formed from hexene-1 under these conditions.

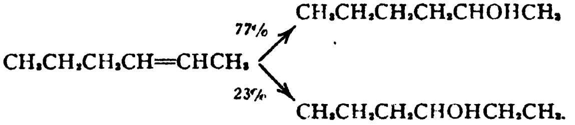
Twelve grams of 2-methylpentene-1 (unsymmetrical n-propylmethylethylene) were treated with 2 volumes of 85 per cent acid at 10° C. The oil lost 55 per cent of its volume by solution. On diluting with iced water, 4.5 grams of a light yellow oil were obtained having a strong camphor-like odor common to all tertiary alcohols. The hydration had evidently resulted in the production of dimethyl-n-propylcarbinol:



From the treatment of 46.5 grams of tetramethylethylene with 150 grams of 85 per cent sulphuric acid at 0° C. for one hour, followed by another hour's standing in which the temperature rose to 15° C., Brooks and Humphrey obtained 37.6 grams of a mixture of hydrocarbons, of which the dimer appeared to be the main constituent. On diluting the acid layer with water, only 1.6 grams of a tertiary alcohol (dimethylisopropylcarbinol) precipitated. The diluted acid liquor, after neutralization with barium carbonate, yielded 20.2 grams of soluble barium salts, accounting for 7.1 grams of the original olefin. Evidently to obtain good yields of the tertiary alcohol, sulphuric acid of considerably lower concentration is necessary.

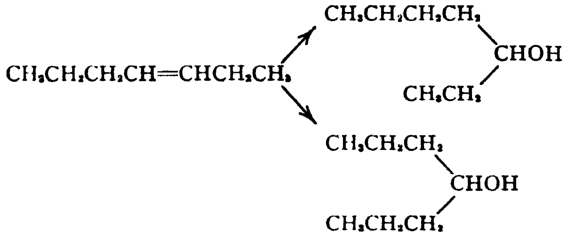
Michael and Brunel observed that tetramethylethylene reacts easily and completely with 77 per cent acid at ordinary temperatures, but not as rapidly as trimethylethylene. The products of the reaction were not, however, examined. The slow hydration of tetramethylethylene, with 5 to 10 per cent aqueous solutions of oxalic acid at 100° C., to dimethylisopropylcarbinol was noted by Miklaschewsky.[40]

According to Michael and Hartman,[41] hexene-2 can react with sulphuric acid in two ways and the hydrolyzed products consist of two isomeric hexyl alcohols in the proportion of 77 per cent of methylbutylcarbinol and 23 per cent of ethylpropylcarbinol, thus



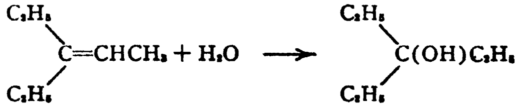
$$CH_3CH_2CH_2CH{=}CHCH_3 \xrightarrow{77\%} CH_3CH_2CH_2CH_2CHOHCH_3$$
$$CH_3CH_2CH_2CH{=}CHCH_3 \xrightarrow{23\%} CH_3CH_2CH_2CHOHCH_2CH_3.$$

The Heptenes. Brooks and Humphrey examined the action of 85 per cent sulphuric acid on 5-methylhexene-1 (iso-α-heptene), heptene-3, and 3-ethylpentene-2. Heptene-3 was remarkable in that it gave no polymers under these conditions. The conversion of heptene-3 into alcohols is apparently more readily effected by the use of benzenesulphonic acid. On adding this olefin to an excess of crystalline benzenesulphonic acid at room temperature, solution took place. After standing for 2 hours, the excess of benzenesulphonic acid was removed from the oily ester by washing with water. Saponification of the benzenesulphonic ester with aqueous sodium hydroxide gives heptyl alcohol, boiling point 134°-136° C. This alcohol probably contains both dipropylcarbinol and ethylbutylcarbinol, produced according to the following scheme:



$$CH_3CH_2CH_2CH{=}CHCH_2CH_3 \longrightarrow \begin{matrix} CH_3CH_2CH_2CH_2 \\ CH_3CH_2 \end{matrix}{>}CHOH$$
$$CH_3CH_2CH_2CH{=}CHCH_2CH_3 \longrightarrow \begin{matrix} CH_3CH_2CH_2 \\ CH_3CH_2CH_2 \end{matrix}{>}CHOH$$

One hundred grams of 3-ethylpentene-2 and 120 grams of sulphuric acid (d 1.84) at 0° C. yielded 21 grams of oil consisting mainly of the dipolymer together with 82 grams of crude alcohol. The latter decomposed during distillation, possessed a strong odor characteristic of a tertiary alcohol, and was probably composed principally of triethylcarbinol.



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}{>}C{=}CHCH_3 + H_2O \longrightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}{>}C(OH)C_2H_5$$

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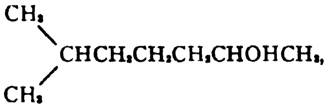
[40] *J. Russ. Phys.-Chem. Soc.*, 1890, 22, 495; *Ber.*, 1891, 24, Ref. 269.
[41] *Ber.*, 1906, 39, 2149.

A further quantity of 6 grams of the tertiary alcohol was recoverable from the diluted acid liquor in the form of its sulphuric ester.

On treating the 5-methylhexene-1 with 85 per cent acid, Brooks and Humphrey obtained a considerable amount of oil consisting mostly of the dipolymer.

HIGHER OLEFINS

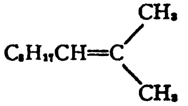
Our knowledge of the action of sulphuric acid on the higher aliphatic olefins is extremely scanty but the work of Brooks and Humphrey indicates that polymerization is always the main reaction. The yields of higher secondary and tertiary alcohols are exceedingly low. Thus, on treating an octene boiling at 122°-124° C. (probably octene-2) with 85 per cent sulphuric acid at 20° C., only a small amount of a secondary octyl alcohol was obtained. Most of the hydrocarbon was converted into polymers. Similarly, 60 grams of α-iso-octene (6-methylheptene-1) and 225 grams of 85 per cent sulphuric acid at 15° C. yielded 48 grams of polymers of which about one-half consisted of the dimer. Only 9 grams of a secondary alcohol, possibly 2-hydroxy-6-methylheptane,



$$\begin{array}{l} CH_3 \\ \quad\diagdown \\ \qquad CHCH_2CH_2CH_2CHOHCH_3, \\ \quad\diagup \\ CH_3 \end{array}$$

were formed.

Brooks and Humphrey also examined the action of 85 per cent acid at 20° C. on 2-methyl-2-undecene,



$$\begin{array}{r} CH_3 \\ \diagup\quad \\ C_8H_{17}CH{=}C\qquad \\ \diagdown\quad \\ CH_3 \end{array}$$

This hydrocarbon was almost entirely converted into a dipolymer with only a trace of higher alcohol. A sample of hexadecene, from spermaceti, was found to be almost unaffected by 85 per cent acid at 20° C., but more concentrated (d 1.84) acid converted it into a mixture of polymers. In general, therefore, it may be concluded that the conversion of the higher olefins into corresponding alcohols by sulphuric acid is a matter of difficulty, probably on account of the instability of these higher alcohols.

INDUSTRIAL METHODS FOR THE PRODUCTION OF HIGHER SECONDARY AND TERTIARY ALCOHOLS

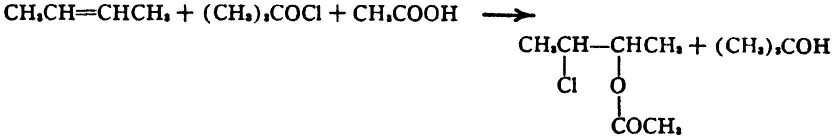
The investigations of Davis and Murray have been referred to in Chapter 14, dealing with the production of isopropyl alcohol. According to the description of the process given in that chapter, three fractions were obtained by the initial fractionation of cracking gas. The treatment of fraction 1, the ethylene-propylene fraction, has been mentioned. Fractions 2 and 3, the butene and pentene (amylene) fractions, will now be discussed.

Fraction 2, containing the isomeric butenes, is first washed with 60 per cent sulphuric acid whereby the highly reactive isobutene is preferentially absorbed. The other two butenes are then absorbed in 80 per cent and at temperatures up to 40° C. (if stronger acid is used the temperature must be maintained below 15° C.). The liquid from the first step, containing tertiary butyl alcohol and its sulphuric ester, is diluted, neutralized with alkali, and distilled to yield the tertiary butyl alcohol. The liquid from the second step is diluted and distilled (without previous neutralization) to give secondary butyl alcohol.

The amylene fraction (fraction 3) consists preponderantly of amylenes with possibly some hexenes and higher olefins, as well as diolefins and less than 5 per cent of paraffins. This liquid may be submitted to a fractional distillation to yield the following fractions: (a) b.p. up to 25° C., mainly isopropylethylene; (b) b.p. 25° to 45° C., consisting of pentene-1, pentene-2, unsymmetrical methylethylethylene, and trimethylethylene; and (c) b.p. above 45° C., containing hexenes and higher olefins. The conversion of isopropylethylene from fraction (a) into an alcohol is not a part of their process. It is stated that by treating fraction (b) with concentrated hydrochloric acid, tertiary amyl chloride is formed together with a mixture of dichloride and unsaturated chlorides (probably derived from admixed diolefins). This mixture may yield, on hydrolysis, tertiary amyl alcohol.[42]

Alternatively the whole of the amylene fraction (3) may be treated with sulphuric acid of 60 per cent strength, which promotes the formation of tertiary alcohols by the hydration of isobutylene, trimethylethylene, and unsymmetrical methylethylethylene, and simultaneously polymerizes the diolefins to heavy oil-like polymers (which may be separated). The unattacked portion of the pentene fraction (a mixture principally of isopropylethylene, pentene-1, and pentene-2) is treated with 77 per cent sulphuric acid, forming the sulphuric esters of secondary amyl alcohols, from which the free alcohols are recovered by dilution and distillation.[43]

Although not strictly within the scope of this chapter it is convenient to mention here a method for the direct esterification of secondary olefins by organic acids.[44] The esterification of secondary olefins of 4 carbon atoms or more with acetic acid or other organic acids proceeds readily at comparatively low temperatures, using equimolecular quantities of reactants, in the presence of catalysts. Sulphuric acid may be used as a catalyst and it is advantageous to add some preformed ester as a solvent. It is interesting to note that butene-2, and other olefins of this type, react with organic acids in the presence of tertiary butyl hypochlorite to yield chloroalkyl esters:



$$CH_3CH{=}CHCH_3 + (CH_3)_3COCl + CH_3COOH \longrightarrow \underset{\displaystyle Cl}{CH_3CH}{-}\underset{\displaystyle \underset{\displaystyle COCH_3}{O}}{CHCH_3} + (CH_3)_3COH$$

Taveau[45] recommended the treatment of olefins, present in cracking gas, and also the volatile liquid products of cracking, with sulphuric acid of various concentrations. The olefin-containing gas is washed with sulphuric acid in a succession of towers so that the olefins are removed successively and a certain degree of separation is effected. Increased pressures may be employed. It is best to allow the acid liquor formed in the absorbing chambers to be diluted immediately as it emerges, either by being poured into water when alcohols are to be produced, or into calcium acetate and water when esters are desired. From cracking gas the various olefins are absorbed in the following order and under the following conditions:

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[42] The preparation of chlorides and chlorohydrins by treating olefin fractions with hydrogen chloride or hypochlorous acid, respectively, is described by Blanchet, British Patent 251,652, 1926; assigned to Soc. Anon. d'Explosifs et de Prod. Chim.; *Brit. Chem. Abs.* **B**, 1927, 836.

[43] For additional information with regard to the production of higher secondary and tertiary alcohols see: Davis, U. S. Patents 1,790,517, 1,790,518, 1,790,519 and 1,790,520, Jan. 27, 1931, U. S. Patent 1,879,660, Sept. 27, 1932; Davis and Harford, U. S. Patent 1,790,521, Jan. 27, 1931; Davis and Murray, U. S. Patents 1,790,522, Jan. 27, 1931; 1,844,209 and 1,844,211, Feb. 9, 1932; all patents assigned to Petroleum Chemical Corp.

[44] Davis and Harford, U. S. Patent 1,790,521, Jan. 27, 1931; assigned to Petroleum Chemical Corp.; *Chem. Abs.*, 1931, **25**, 1375.

[45] Canadian Patent 258,277, 1924; *Brit. Chem. Abs.* **B**, 1927, 378; U. S. Patent 1,810,192, June 16, 1931; *Chem. Abs.*, 1931, **25**, 4557; U. S. Patent 1,845,007, Feb. 16, 1932; *Chem. Abs.*, 1932, **26**, 2200; all assigned to The Texas Company. *Cf.* Markowish and Moor, *Neft. Khoz.*, 1930, **19**, 604; *Chem. Abs.*, 1931, **25**, 3473.

(1) The most reactive olefin, isobutene, is absorbed in 60 to 70 per cent sulphuric acid (best with 65 to 66 per cent) at a temperature not exceeding 30° C.

(2) The isomeric butenes (butene-1 and -2) are absorbed in 80 to 90 per cent acid (best 85 per cent) at a temperature not above 30° C.

(3) Propylene is absorbed in acid of at least 90 per cent concentration, particularly 94 per cent or higher, also at a temperature not above 30° C.

(4) Ethylene is absorbed in highly concentrated acid, such as 98 per cent or higher, at a temperature of 80° to 110° C., and not ordinarily above 120° C.

The corresponding alcohols are made by diluting the acid liquor with 2½ volumes of water at a low temperature and distilling with steam. The resulting distillates from propylene and its homologues separate into two layers, the top layer consisting of water-insoluble alcohols and light polymerization products, and the lower layer of water-soluble alcohols. The top layer must be washed with water to remove any water-soluble alcohols.

Van Peski[46] pointed out that during the absorption of the homologues of ethylene in relatively dilute acid, dilution with ammonium sulphate is equally as efficacious as dilution with water. Since the production of tertiary alcohols always involves the preliminary neutralization of the diluted acid before distillation, this fact is useful in that neutralization may be effected by ammonia (or its salts) with the subsequent formation of ammonium sulphate, part of which is removed and part re-used to dilute more acid. The following example suffices to demonstrate the process: 50.6 grams of 96 per cent sulphuric acid are diluted with 41 grams of an aqueous 40 per cent solution of ammonium sulphate, and a small amount of potassium ferrocyanide added as a catalyst. After dilution, the concentration of the acid is 65 per cent. The acid is brought into contact with 58 grams of technical butene, consisting of 30 per cent of normal butene, 54 per cent of isobutene, and 16 per cent of saturated hydrocarbons. Only the isobutene is absorbed. After absorption the mass is neutralized with 25 per cent aqueous ammonia and distilled, yielding 34.5 grams of pure tertiary butyl alcohol. From the residue, cooled to 0° C., 15 grams of pure ammonium sulphate can be crystallized. The mother liquor (133 grams of 40 per cent ammonium sulphate solution) can be used again for diluting fresh acid. When dilution of the acid is effected with water alone, the other steps being the same, the yield of tertiary alcohol is also 34.5 grams.

Buc[47] obtained reactive acid liquors from mixtures of olefins of different molecular weights by treating them in three successive stages. The concentration of the sulphuric acid in the first stage is below 65 per cent, in the second stage between 78 and 82 per cent, and in the final stage above 90 per cent. The temperature is kept below 120° F. throughout, particularly between 90° and 120° F. in the first and second stages. When gaseous mixtures of olefins are the raw material, a mineral oil, such as gas oil or light lubricating oil, is introduced into each absorption tower. This may be omitted with liquid olefins. This procedure is said not only to minimize polymerization but also to reduce the quantity of acid required. Previously, absorption was always discontinued when about one mole of olefin was absorbed per two moles of acid, but by this method olefins higher in the series than propylene may be absorbed up to about one mole of olefin per mole of acid. After hydrolysis as much as 150 to 170 volumes of higher secondary alcohols per 100 volumes of 80 per cent acid have been obtained and even greater yields of tertiary alcohols.

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[46] British Patent 341,167, 1931; *Brit. Chem. Abs.* **B**, 1931, 334. French Patent 705,172, 1930; *Chem. Abs.*, 1931, **25**, 5175. U. S. Patent 1,884,405, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 992; *cf.* French Patent 716,046, 1931; *Chem. Abs.*, 1932, **26**, 1946; British Patent 360,331, 1931; *Chem. Abs.*, 1933, **27**, 515; French Patent 743,860, 1933; *Chem. Abs.*, 1933, **27**, 4022; all assigned to Bataafsche Petroleum Maatschappij.

[47] British Patent 340,098, 1929; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 192.

The separation of higher alcohols from the polymerized oils simultaneously formed in the sulphuric acid absorption has offered some difficulty. According to Merley,[48] the alcohols are separated from such oils by using benzenesulphonic acid and a water-soluble alcohol (e.g., isopropyl alcohol) as a selective solvent. This procedure is applicable to the separation of hexyl, or other heavy alcohols, from polymerized oils.

The Bataafsche Petroleum Maatschappij[49] converted cyclic olefins into the corresponding alcohols by treatment with 80 per cent sulphuric acid at low temperatures in the presence of catalysts (ferricyanic acid). The acid liquor (after absorption of the olefin) is poured into iced water, neutralized with alkali and distilled. An example is the conversion of cyclohexene into cyclohexanol.

Brooks[50] recovered alcohols of three to six carbon atoms from the diluted acid liquor polymers by distilling a part of the polymer layer. The alcohols were found in the first runnings. Distillation with steam, according to Brooks, gives a larger yield of alcohols, apparently due to reaction of the steam with certain bodies present in the polymer layer.

SUMMARY

(1) The higher homologues of ethylene show an increasing reactivity toward sulphuric acid with increasing molecular weight, this reactivity apparently being at a maximum with the pentenes and hexenes. Beyond this point olefins of greater molecular weight show a decreasing reactivity toward sulphuric acid.

(2) Direct esterification of the homologues of ethylene is complicated by polymerization and condensation. The tendency toward polymerization is, in general, most pronounced with concentrated sulphuric acid and at higher temperatures. To obtain good yields of alcohols it becomes necessary, therefore, to use acid of as low a concentration as possible (60 per cent or lower in the case of the iso-hydrocarbons) and also to maintain the temperature of the reaction mixture at a low point. Under these conditions there is much evidence to support the conclusion that the dilute acid reacts as a hydrating catalyst, the alkylsulphuric acids being afterwards formed by the esterification of the alcohol. It has also been assumed that esters of hydrated sulphuric acid are first produced and that these are readily hydrolyzed to alcohols. In the case of tertiary alcohols from iso-olefins, direct hydration appears to be the predominating reaction.

(3) The lower olefins vary enormously in their reactivity with sulphuric acid.

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[48] U. S. Patent 1,732,903, Oct. 22, 1929; assigned to Doherty Research Co.; *Chem. Abs.*, 1930, **24**, 130. See also U. S. Patent 1,897,812, Feb. 14, 1933; assigned to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 2696; Nametkin and Abakumuvskaja, *Ber.*, 1933, **66**, 358; *Brit. Chem. Abs.* **A**, 1933, 385.

[49] British Patent 339,592, 1931; *Brit. Chem. Abs.* **B**, 1931, 334. See also British Patent 323,748, 1929; *Brit. Chem. Abs.* **B**, 1930, 359; British Patent 381,723, 1931; *Brit. Chem. Abs.* **B**, 1933, 10; French Patent 730,829, 1932; *Chem. Abs.*, 1933, **27**, 305; French Patent 700,067, 1930; *Chem. Abs.*, 1931, **25**, 3358. The absorption of carbon monoxide and diolefins was also described by the Bataafsche Petroleum Maatschappij (French Patent 705,214, 1931; *Chem. Abs.*, 1931, **25**, 5223).

[50] U. S. Patent 1,944,400, Jan. 23, 1934; assigned to Standard Alcohol Co.

The iso-olefins are by far the most reactive in the order: isobutene, trimethylethylene, and unsymmetrical methylethylethylene. Next come isopropylethylene, butene-2, butene-1, pentene-2, pentene-1, and finally propylene. The great differences in the rates of absorption may be utilized to effect a partial separation. Thus, the three above-mentioned "tertiary" olefins (i.e., olefins yielding tertiary alcohols on hydration) may be separated more or less completely from secondary olefins by treating mixtures with 60 to 70 per cent acid at 20° C. The more reactive secondary olefins (butene-1, butene-2, pentene-1, pentene-2) are removed from admixed propylene by 80 per cent sulphuric acid at temperatures below 30° C.

(4) The secondary olefins of four and five carbon atoms (excepting isopropylethylene) are easily converted into sulphated materials by approximately 80 per cent acid at 20° C. with relatively little polymerization. The tertiary olefins may be hydrated by 60 per cent acid (or less) also at low temperatures (20° C.). Apparently isopropylethylene is polymerized by sulphuric acid of 80 per cent concentration and over and unaffected by acid of less concentration, so that it is impossible in this manner to prepare the corresponding alcohol in any quantity.

(5) For the treatment of olefins with sulphuric acid, countercurrent scrubbing in towers is usually recommended for gaseous olefins. Liquid olefins are generally agitated with acid in a tank fitted with necessary cooling devices. In treating gaseous olefins, the addition of a neutral liquid diluent (mineral oil) having a solvent action on the olefin is beneficial.

(6) The methods adopted for working up the acid liquor vary in accordance with the character of the alcohol to be recovered. It appears fundamental that tertiary alcohols must be distilled from neutral or slightly alkaline solutions because of the ease with which dehydration proceeds, in the presence of even dilute acids. It is therefore necessary to neutralize the acid liquor with sodium hydroxide, lime, or aqueous ammonia, before distilling off the alcohol. It is usually sufficient to dilute the acid liquor containing secondary alcohols with several times its volume of cold water before distillation.

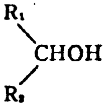
Chapter 17

Properties and Uses of Higher Secondary and Tertiary Alcohols Derived from Olefins

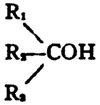
The alcohols obtained by the hydration of the homologues of ethylene are secondary and tertiary compounds in sharp contrast to those produced by fermentation processes which are almost exclusively primary products. These three types of alcohols differ markedly in chemical and physical properties on account of the following characteristic groupings:

RCH_2OH

Primary



Secondary



Tertiary

The divergence in chemical properties associated with their different structures is well exemplified by their behavior on oxidation. When subjected to oxidation the primary alcohols initially yield aldehydes with the same number of carbon atoms and secondary alcohols are readily oxidized to ketones, also with the same number of carbon atoms as the parent alcohol. Tertiary alcohols are characterized, however, by a relatively great resistance to oxidizing agents. When oxidation does occur, a breakdown of the alcohol molecules takes place with the formation of oxidized products of lower molecular weight than the parent alcohol. The marked stability of tertiary alcohols to oxidation is shown by the fact that these alcohols when treated with chromic anhydride form esters of chromic acid, a reaction first investigated by Wienhaus.[1] Another instance of the different chemical natures of these three types of alcohols is their relative ease of dehydration to olefins.[1a] Tertiary alcohols are readily dehydrated to the corresponding (tertiary) olefin by warming with dilute mineral acids and, for this reason, tertiary alcohols cannot be distilled from the diluted acid liquor made by dissolving tertiary olefins in 60 per cent sulphuric acid. Even oxalic acid can dehydrate these alcohols. For example, good yields of isobutylene are obtained by warming tertiary butyl alcohol with oxalic acid. In this reaction stronger acids, such as sulphuric acid, not only dehydrate the tertiary alcohol but tend to polymerize the resulting olefin. Thus, if the alcohol is distilled from sulphuric acid solutions, the relative proportions of the olefin and of its polymers depend upon the quantity and concentration of the acid and upon the conditions of distillation. Primary and secondary alcohols are less readily dehydrated than tertiary alcohols.

Tertiary alcohols are distinguished by the ease with which they combine with halogen acids to form alkyl esters. For instance, when tertiary butyl alcohol is treated with concentrated hydrochloric acid at ordinary temperatures it is converted into the tertiary butyl chloride, which separates immediately. This fact has been made the basis of a test to distinguish these three classes of alcohols. Secondary, but not primary, alcohols are converted into alkyl chlorides by concentrated hydrochloric acid containing zinc chloride.[2] In this, as in other chemical and physical properties, the secondary alcohols occupy a position intermediate between primary and tertiary alcohols. The lability of the hydroxyl group in the tertiary alcohols is inherited by the acid radical which displaces it. Thus secondary butyl chloride is partly hydrolyzed by water and tertiary butyl bromide is converted into the alcohol by cold water. The iodide reacts even more readily and boiling water converts it into isobutylene, simultaneous hydrolysis and dehydration taking place. The remarkable ease with which the tertiary alcohols combine with even weak inorganic acids is exemplified by the ready formation of tertiary alkyl hypochlorites by treatment with aqueous hypochlorous acid.[3]

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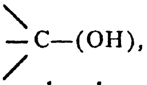
[1] *Ber.*, 1914, 47, 322.

[1a] Whitmore and his collaborators (results reported in *J.A.C.S.*) conducted extensive studies of the dehydration and molecular rearrangement of numerous alcohols.

As distinguished from secondary and primary alcohols, the tertiary alcohols cannot be esterified directly by organic acids, such as acetic acid. Indirect methods must be adopted to obtain these esters, which are very readily hydrolyzed. Tertiary alcohols and acid chlorides, such as acetyl chloride, do not yield organic esters but rather the tertiary alkyl chlorides, in sharp contrast to the behavior of secondary and primary alcohols.

Of the three classes of alcohols, the secondary ones are the most reactive to halogens on account of their reactive hydrogen attached to the alcoholic group. Next in order of reactivity come the primary alcohols, and the tertiary bodies are the most stable toward halogens since they do not contain a hydrogen atom attached to the C—OH group. Davis and Murray[4] reported that solutions of bromine in tertiary butyl alcohol have been used as a laboratory reagent and are quite stable, even in sunlight, but decompose at 80° to 90° C. Tertiary amyl alcohol is also comparatively stable to bromine but the solution is rapidly decolorized at 80° C.

The chemical properties of tertiary alcohols can be understood on the assumption that the bond between the tertiary carbon atom and the hydroxyl group,  $\begin{matrix}\diagdown & & \\ - & C & -(OH) \\ \diagup & & \end{matrix}$, is relatively weak because the valences of the central carbon atom are largely satisfied by the other three radicals attached to this atom. Since this carbon-oxygen linkage is weak the bond O—H is abnormally strong. The stability of this O—H bond is strikingly shown by the behavior of the tertiary alcohols with metals and metallic oxides. Metallic sodium reacts only slowly with tertiary butyl alcohol even at the boiling point of that alcohol. Barium oxide, also, gives no alcoholate so that this tertiary alcohol may be safely dehydrated over these substances. Neither barium oxide nor sodium can be used to dehydrate hexyl and higher tertiary alcohols because of the formation of resins, but tertiary amyl alcohol is stable toward these substances up to about 102° C.

In physical, as well as chemical, characteristics these three types of alcohols show a gradation of properties, the secondary alcohols occupying a position intermediate between the primary and the tertiary. The boiling point and density of tertiary butyl alcohol are approximately the same as that of isopropyl alcohol or of ethyl alcohol. It appears to be a fairly general rule that the physical properties of a tertiary alcohol are similar to those of the homologous secondary alcohol with one less carbon atom in its molecule and of the primary alcohol with two carbon atoms less. The solubilities of the three types of alcohols in water follow the same rule to some extent, but no such similarity exists in the case of refractive indices or freezing points.

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[2] Lucas, *J.A.C.S.*, 1930, **52**, 802.

[3] Chattaway and Backeberg, *J.C.S.*, 1923, **123**, 2999.

[4] *Ind. Eng. Chem.*, 1926, **18**, 844.

Tests for Distinguishing the Three Types of Alcohols

The most convenient method of distinguishing between the three classes of aliphatic alcohols is that given by Kamm,[5] who made use of the difference in the rate with which the alcohols react with hydrobromic acid. The tertiary alcohols react most readily, and the secondary alcohols occupy an intermediate position. Lucas[6] developed a test which consists in treating the alcohol with concentrated hydrochloric acid. Tertiary alcohols immediately react to form insoluble chlorides which rise to the surface in a few minutes. The residual liquid containing, possibly, both secondary and primary alcohols is treated at 26° to 27° C. with about 6 times its volume of a reagent made by dissolving 136 grams of anhydrous zinc chloride in 105 grams of concentrated hydrochloric acid. Under these conditions secondary alcohols yield alkyl chlorides and, on standing, the clear solution becomes cloudy within five minutes. If no change, other than darkening, is observed then secondary alcohols are absent.

Wienhaus[7] described a useful test for some tertiary alcohols. This is based upon their combination with chromic acid. A solution of the substance under examination in carbon tetrachloride or petroleum ether develops a pure red color when shaken with aqueous chromic acid if it contains tertiary alcohols. If the solution rapidly discolors, however, tertiary alcohols are not entirely excluded since these often undergo oxidation. Other methods for the identification of alcohols are given by Shriner and Cox,[7a] Morgan and Pettet,[7b] and Weber and Koch.[7c]

Pharmacology of the Three Classes of Alcohols

Our knowledge of the physiological action of the higher alcohols is rather inadequate but it is generally agreed that toxicity in a homologous series of alcohols, as well as narcotic action, increases with increasing molecular weight.[8] Increase in narcotic action is more rapid than in toxicity. The same increase of toxicity of aliphatic alcohols with increasing molecular weight has been noted in the action of alcohols on spores.[9]

Weese[10] exposed white mice to vapors of aliphatic alcohols at constant temperature with equimolecular amounts volatilized in a constant space. When the air was saturated with alcohol vapors the narcotic and toxic effects increased with the number of carbon atoms in the alcohol molecule. In an atmosphere which was not saturated with alcohol vapors the relationship was somewhat changed, in that n-butyl and isobutyl alcohols were less active as narcotics than propyl alcohol, while secondary and tertiary butyl alcohols were more effective.

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[5] Kamm and Marvel, *J.A.C.S.*, 1920, **42**, 299; Kamm, "Qualitative Organic Analysis," Wiley and Sons, Inc., 1923.

[6] *J.A.C.S.*, 1930, **52**, 802.

[7] *Ber.*, 1914, **47**, 322.

[7a] *J.A.C.S.*, 1931, **53**, 1601.

[7b] *J.C.S.*, 1931, 1124.

[7c] *Chem. Ztg.*, 1933, **57**, 73; *Brit. Chem. Abs.* **B**, 1933, 215.

[8] Munch and Schwartze, *J. Lab. Clin. Med.*, 1925, **10**, 985; *Chem. Abs.*, 1926, **20**, 1851; *J. Pharmacol.* (*Proc.*), 1922, **19**, 252. The pharmacology of isopropyl alcohol is discussed in Chapter 15.

[9] Uppal, *J. Agric. Res.*, 1926, **32**, 1069; *Chem. Abs.*, 1926, **20**, 2716.

[10] *Arch. Exptl. Path. Pharm.*, 1928, **135**, 118; *Chem. Abs.*, 1929, **23**, 908.

The toxicity of tertiary butyl alcohol falls between that of n-propyl and n-amyl alcohols, and of n-butyl alcohol, between ethyl and methyl alcohols.

Measurements of the toxicity of various aliphatic alcohols toward guinea pigs, rabbits, and other animals were made by Rost and Braun.[11] The alcohols were usually administered orally, but also sometimes by injection or inhalation. The effect was qualitatively the same but quantitatively it increased with increasing molecular weight. The study of n-butyl, and secondary butyl, alcohols was complicated by their slight solubility.

SECONDARY BUTYL ALCOHOL (BUTANOL-2)

Secondary butyl alcohol, formed by the hydration of both butene-1 and butene-2, is a colorless liquid possessing a strong, pleasant odor and is without choking action on the bronchial tubes. It has boiling point 99.5° C. (760 mm.), d_4^{25} 0.8022, n_D^{15} 1.3974 and is soluble in 8 volumes of water at 20° C. It forms a constant-boiling mixture with water boiling at 87.5° C. (760 mm.) and having the composition 72.7 per cent of alcohol and 27.3 per cent water. The alcohol also forms a constant-boiling mixture with its acetic ester, containing 13.7 per cent of secondary butyl acetate, and boiling at 99.6° C. The secondary alcohol is, for all practical purposes, non-toxic. It is a solvent for ester gum, shellac, and other gums, castor and linseed oils, and aromatic hydrocarbons, but not for cellulose esters. Although not a satisfactory substitute for normal butyl alcohol in all cases, it is of importance in the lacquer industry mainly in the form of its acetic ester. On treating secondary butyl alcohol with carbon disulphide and sodium hydroxide a xanthate forms which is suggested as a flotation agent, insecticide and vulcanization accelerator.[11a]

The purification of secondary butyl alcohol, made from butylenes in cracking gas, has been the subject of a number of investigations. Lebo[12] proposed to separate the secondary alcohols from admixed isopropyl alcohol, by treatment with benzene, which forms a low-boiling azeotropic mixture with isopropyl alcohol. Merley[13] suggested extracting the diluted acid liquor with water-insoluble, straight-chain hydrocarbons. The latter, together with the dissolved polymers, are removed before distillation of the liquor. Mann[14] dehydrated secondary butyl alcohol by mixing the crude alcohol with a hydrocarbon oil having a high initial boiling point; for example, gas oil of initial boiling point 350° F., mineral seal of initial boiling point of 405° F., or a heavier lubricating oil. On allowing the mixture to separate, the upper layer contains alcohol and oil with a small amount of water and the lower layer consists of water and a small amount of alcohol. By varying the proportion of oil used the extent of dehydration may be varied between wide limits.

Apparently secondary butyl alcohol itself may be used as a dehydrating agent[15] for a number of substances, such as secondary amyl, hexyl and heptyl alcohols. The secondary alcohol forms a constant-boiling mixture with water having the composition by volume of 22 parts of water and 78 parts of alcohol, so that comparatively small amounts of butyl alcohol are required to take up large proportions of water from the higher-boiling liquid. The use of secondary butyl alcohol for dehydrating cellulose nitrate has been described by Wiesel.[16]

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[11] *Arb. Reichgesundh.*, 1926, **57**, 580; *Chem. Abs.*, 1927, **21**, 2738.

[11a] Christmann and Jayne, U. S. Patent 1,810,552, June 16, 1931; assigned to American Cyanamid Co.; *Chem. Abs.*, 1931, **25**, 4559; Bataafsche Petroleum Maatschappij, British Patent 377,077, 1931; *Brit. Chem. Abs.* **B**, 1932, 973.

[12] U. S. Patent 1,422,583, July 11, 1922; *Chem. Abs.*, 1922, **16**, 3093; U. S. Patent 1,911,829, May 30, 1933; *Chem. Abs.*, 1933, **27**, 3943; both assigned to Standard Oil Development Co.

[13] U. S. Patent 1,713,346, May 14, 1929; assigned to Doherty Research Co.; *Chem. Abs.*, 1929, **23**, 3341. See also U. S. Patent 1,835,571, Dec. 8, 1931; *Brit. Chem. Abs.* **B**, 1933, 218; U. S. Patent 1,873,006, Aug. 23, 1932; *Chem. Abs.*, 1932, **26**, 5963; U. S. Patent 1,933,505, Oct. 31, 1933; all assigned to Doherty Research Co.

[14] U. S. Patent 1,524,192, Jan. 27, 1925; *J.S.C.I.*, 1925, 265B; Canadian Patent 257,750, 1926; *Chem. Abs.*, 1926, **20**, 2333; both patents assigned to Standard Oil Development Co.

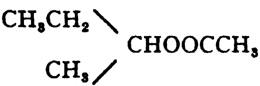
[15] Merley, U. S. Patent 1,688,731, Oct. 23, 1928; assigned to Doherty Research Co.; *Chem. Abs.*, 1929, **23**, 155.

ESTERS OF SECONDARY BUTYL ALCOHOL

The most important ester of secondary butyl alcohol is the acetate, which is made on a considerable scale by direct esterification. A process developed by Buc and Clough[17] involves the distillation of a mixture of about 55 per cent of commercial secondary butyl alcohol (as it comes from the finishing run without total dehydration), 45 per cent of strong acetic acid (which need not be glacial but should be of at least 75 per cent concentration) and about 0.1 per cent of sulphuric acid. The upper layer settling from the condensate is refluxed continuously until stratification ceases. The still contents are then distilled, the first fraction boiling within a few degrees of the boiling point of the secondary ester being added to the next batch charge. The second and main fraction, boiling up to within two or three degrees of the boiling point of acetic acid, consists mainly of the desired ester but containing 15 to 30 per cent of acetic acid. The residue in the still, mainly acetic acid, is used in the next operation. The second (or ester) fraction is now subjected to fractional distillation, after addition of sufficient water to form a constant-boiling mixture with the ester. If the water fractionation is carried out carefully, the ester distils over with very little acetic acid. It is then submitted to final purification.

The esterification of secondary butyl and amyl alcohols by organic acids (e.g., acetic acid) can be accomplished in the presence of a solvent in which the solubility of the ester is greater than that of its components or of water.[18] Such a solvent material is a white petroleum fraction of initial boiling point 300° C. and d 1.247.

It is interesting to note in this connection, that when an alcohol, together with the ester of a second alcohol, is passed in the vapor state over an alumina catalyst, partial replacement of the alcohol radical in the ester occurs with the formation of a mixture of esters.[19] Methyl formate and isobutyl alcohol vapors conducted over alumina at 150° C. are converted to the extent of 20 to 30 per cent into isobutyl formate and methyl alcohol.

Secondary butyl acetate having the formula  $\begin{matrix}CH_3CH_2\diagdown \\ CH_3\diagup\end{matrix}CHOOCCH_3$, is a colorless liquid (boiling point 112.2° C.) and is more soluble in water than normal butyl acetate. It possesses a pleasant fruity odor, exerts no choking action on the bronchial tubes, and is considered non-toxic.[20] It is a solvent for cellulose nitrate and for many gums (ester gum, mastic, kauri and benzyl abietate, but it only partly dissolves shellac and dammar). The ester is miscible with castor and linseed oils and hydrocarbons. Cellulose acetate does not dissolve in this ester.[21] Secondary butyl acetate is finding a distinct use in the preparation of lacquers, both as a base solvent and as a thinner.[21a]

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[16] British Patent 293,291, 1927; assigned to Hercules Powder Co.; *Chem. Abs.*, 1929, 23, 1750.

[17] U. S. Patent 1,726,945, Sept. 3, 1929; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1929, 23, 5196.

[18] Buc, U. S. Patent 1,651,666, Dec. 6, 1927; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1928, 22, 788. See also British Patent 305,308, 1927; *Chem. Abs.*, 1929, 23, 4709.

[19] I. G. Farbenindustrie A.-G., German Patent 434,400, 1924; *Brit. Chem. Abs.* B, 1927, 348. See also Dr. A. Wacker Ges. für elektrochemische Ind., G.m.b.H., British Patent 387,621, Oct. 19, 1932; *Brit. Chem. Abs.* B, 1933, 296; Norris and Rigby, *J.A.C.S.*, 1932, 54, 2088; *Brit. Chem. Abs.* A, 1932, 718; Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, British Patent 362,458, 1930; *Brit. Chem. Abs.* B, 1932, 332.

[20] The secondary butyl acetate formerly manufactured possessed a disagreeable odor caused by impurities.

A study of the secondary alkyl acetates and their uses in the production of lacquers was made by Park and Hopkins,[22] who emphasized their importance to that industry. The secondary butyl acetate examined by these workers had the following composition and properties: concentration of ester, 85-88 per cent; boiling point 107°-114° C.; $d_{15.5}^{15.5}$ 0.861, n_D^{20} 1.3915. It was an excellent solvent for cellulose nitrate, being intermediate between n-butyl acetate and n-butyl propionate, and somewhat superior to "Pentacetate." [23] The solubility of the ester in water at 25° C. was 1.0 cc. per 100 cc. of water, the corresponding figure for the normal ester being 0.7 cc. Its evaporation rate was intermediate also between that for isopropyl and n-butyl acetate. In blush resistance in lacquers, the secondary butyl ester is similar to the normal butyl compound.

Secondary butyl formate was found by Cotton and Roark [24] to be decidedly toxic, like other alkyl formates, to different kinds of insects and hence to be useful as a fumigant. According to Nelson,[25] secondary butyl formate has a boiling point of 93.6° C. (760 mm.) and its vapor pressure variation with temperature can be represented by the formula:

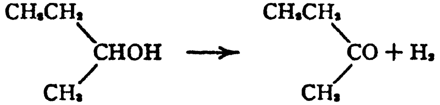
$$\log_{10} P = 8.0306 - \frac{1888.9}{T\ (\text{abs.})}$$

Similarly, secondary butyl chloroacetate, as well as other alkyl chloroacetates, as fumigants were investigated with encouraging results.[26] This ester boils at 167.5° C. (760 mm.) and its vapor pressure has been determined over a wide temperature range.[27]

A possible application of some of the esters of secondary butyl alcohol is in the manufacture of perfumes and flavoring materials.

OXIDATION OF SECONDARY BUTYL ALCOHOL

The oxidation of secondary butyl alcohol offers a convenient method for the preparation of methyl ethyl ketone, an excellent solvent which can replace acetone for many purposes. The reaction is carried out either by catalytic dehydrogenation or by partial oxidation, and may be represented as follows:



$$(CH_3CH_2)(CH_3)CHOH \longrightarrow (CH_3CH_2)(CH_3)CO + H_2$$

Oxidation may be effected by a silver catalyst and dehydrogenation occurs in the presence of reduced copper, other catalysts having been used successfully in both reactions. Thus by the catalytic oxidation of secondary butyl alcohol by air at 335° to 340° C. over a zinc oxide catalyst, Ottensooser [28] obtained a 93 per cent conversion into the corresponding ketone. As an industrial process, it has been proposed to pass the air-alcohol mixture in vapor form over a catalyst heated to at least 500° C., the heat of reaction being sufficient to maintain the desired temperature. Copper, either alone or alloyed with other metals such as zinc, has been suggested as a catalytic material.[29]

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[21] Durrans, "Solvents," Chapman and Hall, London, 1930.

[21a] See Martin, *Metal Cleaning and Finishing*, 1933, 5, 27; *Chem. Abs.*, 1933, 27, 1772.

[22] *Ind. Eng. Chem.*, 1930, 22, 826.

[23] "Pentacetate" is a mixture of the acetates derived from the three primary and two secondary amyl alcohols. The production and properties of this material are discussed in Chapter 33.

[24] *Ind. Eng. Chem.*, 1928, 20, 380.

[25] *Ind. Eng. Chem.*, 1928, 20, 1382.

[26] Roark and Cotton, *Ind. Eng. Chem.*, 1928, 20, 512.

[27] Nelson, *Ind. Eng. Chem.*, 1928, 20, 1380.

[28] *Bull. soc. chim.*, 1927, (4) 41, 324; *Chem. Abs.*, 1927, 21, 2089.

TERTIARY BUTYL ALCOHOL (TRIMETHYLCARBINOL)

This alcohol, produced industrially by the hydration of isobutylene, is a solid at ordinary temperatures and possesses the typical camphoraceous odor characteristic of tertiary alcohols. When pure it has melting point 25.45° C.,[30] boiling point (760 mm.) 82.55° C.,[31] and d^{20}_{4} 0.7887. The vapor pressure of a very pure specimen (freezing point, 25.50° C.) of the alcohol was determined by Parks and Barton[32] over a temperature range of 20° to 80° C., with the results given in Table 87.

TABLE 87.—*Vapor Pressure of Tertiary Butyl Alcohol.*

Temperature ° C.	Vapor Pressure mm.	Temperature ° C.	Vapor Pressure mm.
20.00	30.6	60.00	285.2
25.00	42.0	65.00	358.2
30.00	56.9	70.00	447.3
35.00	76.3	75.00	553.2
40.00	102.3	80.00	679.4
45.00	133.8	85.00	826.3
50.00	174.3	90.00	996.2
55.00	224.2		

From these figures the boiling point at 760 mm. is deduced to be 82.86° C. Fundamental thermal data relating to this and other alcohols have been published by Parks, Kelley and Huffman.[33]

Tertiary butyl alcohol is miscible with water in all proportions and forms with it a constant-boiling mixture[34] (boiling point 79.9° C. (760 mm.)) of the composition 88.24 per cent alcohol and 11.76 per cent water, having d^{0}_{4} 0.8304.

Tertiary butyl alcohol is a typical tertiary alcohol, notably in the following particulars:

(1) It is comparatively resistant to oxidation but, under strongly oxidizing conditions. it breaks down to form acetone, carbon dioxide and acetic acid.[35]

(2) It is stable toward halogens.

(3) It is very readily dehydrated by even mild agents such as oxalic acid to yield isobutylene.

(4) It yields halides with remarkable ease on treatment with halogen acids even in the cold. On the other hand, it cannot be directly esterified by organic acids, and organic acid chlorides react with it to form tertiary butyl chloride and the organic acid.

(5) The organic esters of this alcohol are readily hydrolyzed by water even in the cold. Also, the tertiary halides are hydrolyzed readily. If the mixture is warmed the tertiary alcohol so formed undergoes dehydration in the presence of the halogen acid. In this way isobutylene can be prepared from tertiary butyl iodide.[36]

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[29] Williams and Haller, U. S. Patent 1,450,569, April 3, 1923; *Chem. Abs.*, 1923, **17**, 2428; Williams and White, U. S. Patent 1,460,876, July 3, 1923; *Chem. Abs.*, 1923, **17**, 2887. Wells, U. S. Patent 1,497,817, June 17, 1924; *Chem. Abs.*, 1924, **18**, 3194.

[30] De Forcrand, *Compt. rend.*, 1903, 136, 1034; *Chem. Soc. Abs.*, 1903, **84** (1), 455.

[31] Davis and Murray, *Ind. Eng. Chem.*, 1926, **18**, 844.

[32] *J.A.C.S.*, 1928, **50**, 24.

[33] *J.A.C.S.*, 1929, **51**, 1969.

[34] Davis and Murray, *loc. cit.*

[35] Butlerow, *Z. Chem.*, 1871, **7**, 485; *Chem. Zentr.*, 1872, 100.

[36] Chechoukoff, *J. Russ. Phys.-Chem. Soc.*, 1885, 17, 56; *Chem. Soc. Abs.*, 1885, **48**, 495.

Large quantities of the tertiary alcohol can and have been produced from cracking gas. The great difficulty is to find an outlet for comparatively large amounts of the material. As far as known, tertiary butyl alcohol, as such, has found no extensive applications in the chemical industry, although it can be used for purifying certain substances (for example, the hydroxy acids) by recrystallization from hot solutions. For this purpose a solvent is needed in which the solubility, though low at ordinary temperatures, increases rapidly with rising temperature. A comparison of the effect of temperature on the solubilities of citric acid in water, ethyl alcohol and tertiary butyl alcohol, respectively, indicates that the latter is by far the superior solvent for recrystallizing this acid.[37]

Souther and Gruse[38] investigated the use of higher secondary and tertiary alcohols (having 3 to 6 carbon atoms), and also of the higher primary alcohols, for the purification of slack wax. They found that such alcohols, either individually or mixed with each other, had a preferential solvent action for the oil admixed with the crude wax. Thus, the commonly employed and time-consuming sweating process might be avoided. The slack wax is comminuted with the alcohol for about five minutes, generally at 80° F. to raise the melting point of the final product, and then pressed in a filter press or run through a centrifuge. The resulting wax cake is again mixed with the alcohol or alcohol mixture (n-butyl alcohol having proved especially efficient for this purpose) and centrifuged. If necessary, the last remaining traces of oil can be removed by further treatment with the solvent. Bradley[38a] suggested as a paint-removing composition a mixture containing a wax and tertiary butyl alcohol. The use of tertiary aliphatic alcohols in fuels for internal-combustion engines has been proposed by Van Schaack.[38b]

From the viewpoint of chemical synthesis, tertiary butyl alcohol offers many interesting possibilities. It may be used for introducing the tertiary butyl group, $(CH_3)_3C-$, into organic compounds, especially into aromatic compounds. Nitrated aromatic hydrocarbons and ketones containing this tertiary alkyl group frequently possess a strong musk-like odor and are valuable in the perfume industry.

Tertiary butyl alcohol is a safe material to handle but possesses a slight narcotic action when taken internally, being excreted in the urine in combination with glycuronic acid.[39]

DERIVATIVES OF TERTIARY BUTYL ALCOHOL

Tertiary Butyl Halides. All the halides of tertiary butyl alcohol are readily prepared by mixing the halogen acid (in the form of a concentrated aqueous solution) with the alcohol in the cold, the ester separating as a top layer in a few minutes. The tertiary halides are also made by the direct combination of isobutylene with the anhydrous halogen acid.[40] Tertiary butyl chloride is a colorless liquid boiling at 51.5° C., and the boiling points of the bromide and iodide are 72° C. and 103° C., respectively. From an industrial point of view the chloride only need be considered. The important application of this material will probably be for introducing the tertiary butyl group into organic compounds, especially aromatic hydrocarbons, by the Friedel-Crafts reaction.

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[37] Davis and Murray, *Ind. Eng. Chem.*, 1926, 18, 844.

[38] U. S. Patent 1,685,058, Sept. 18, 1928; assigned to Gulf Refining Co.

[38a] U. S. Patent 1,901,728, Mar. 14, 1933; assigned to Chadeloid Chemical Co.; *Chem. Abs.*, 1933, 27, 3301.

[38b] U. S. Patent 1,907,309, May 2, 1933; *Chem. Abs.*, 1933, 27, 3587.

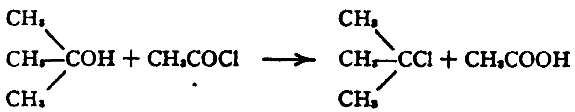
[39] Thierfelder and von Mering, *Z. physiol. Chem.*, 9, 511; *Chem. Soc. Abs.*, 1885, 45, 1002.

[40] For the direct addition of hydrogen chloride to pentenes in the presence of stannic chloride or zinc chloride as a catalyst, see Piotrowski and Winkler, *J. Inst. Pet. Tech.*, 1931, 17, 225.

Tertiary Butyl Hypochlorite. In comparison with primary and secondary alkyl hypochlorites the hypochlorite esters of tertiary alcohols are relatively stable. These substances are yellow, mobile liquids of strong, irritating odor and are prepared by passing chlorine into an ice-cold solution of aqueous sodium hydroxide in the alcohol (the solution should be homogeneous) until absorption ceases. The hypochlorite ester separates.[41]

Tertiary butyl hypochlorite, boiling point 79.6° C., d^{18}_{4} 0.9583, may be distilled without change and, unless exposed to sunlight, kept for months at ordinary temperatures with scarcely any decomposition. When exposed to bright sunlight it decomposes to methyl chloride and acetone. Like all tertiary esters, it can be readily hydrolyzed in dilute alkaline solution.

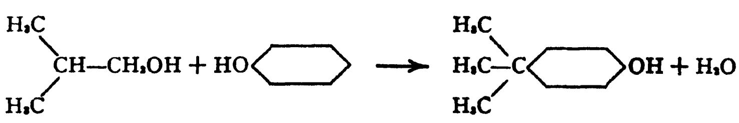
Tertiary Butyl Esters. Esters of tertiary butyl alcohol (and of other tertiary alcohols) appear to be of little promise industrially. They are not readily prepared by the ordinary esterification methods since organic acids dehydrate the alcohols to olefins, and organic chlorides react to form the tertiary alkyl chloride, thus:



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3{-}COH}\\ \mathrm{CH_3}\end{matrix} + \mathrm{CH_3COCl} \longrightarrow \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3{-}CCl}\\ \mathrm{CH_3}\end{matrix} + \mathrm{CH_3COOH}$$

Tertiary butyl acetate, obtained by the direct combination of ketene[42] with the tertiary alcohol, is a liquid (boiling point 96° C.), possessing a somewhat fruity odor, but readily hydrolyzed by water even in the cold.[43]

Other Important Derivatives of Tertiary Butyl Alcohol. Two products which are finding satisfactory application in the commercial production of phenol-aldehyde oil-soluble resins[43a] are para-tertiary-butyl- and amyl-phenol.[43b] The production of these alkylated phenols by addition of olefins to phenol is described in Chapter 24. Nevertheless, they can be made from tertiary alcohols. The alkylation was effected by Liebmann[43c] by heating phenol with an alcohol in the presence of a large excess of a dehydrating agent such as zinc chloride at 180° C. Thus, by heating isobutyl alcohol and phenol, in the presence of zinc chloride, the following reaction occurs:



Other dehydrating agents, for example, acid sulphates,[43d] sulphuric acid,[43e] and perchloric acid,[43f] have also been suggested.

Phenols can be alkylated by using an alkyl halide in the presence of a metallic halide such as aluminum chloride, ferric chloride, or zinc chloride. In the preparation of para-tertiary-butylphenol, for example, tertiary butyl chloride and phenol are reacted in the presence of a small amount of ferric chloride.[43g] This reaction, which can be represented by the equation

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[41] Chattaway and Backeberg, *J.C.S.*, 1923, 123, 2999.

[42] Ketene is described in Chapter 18.

[43] Davis and Murray, *Ind. Eng. Chem.*, 1926, 18, 844.

[43a] The manufacture of synthetic resins from these materials is described by Hönel, French Patent 676,456, 1929; *Chem. Abs.*, 1930, 24, 3092. See also Ellis, *Ind. Eng. Chem.*, 1933, 25, 125; *ibid.*, 1934, 26, 37.

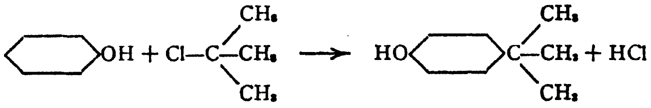
[43b] Para-tertiary-amylphenol is known in the trade as Pentaphen (Sharples Solvents Corp.).

[43c] *Ber.*, 1881, 14, 1844; *ibid.*, 1882, 15, 150. See A.-G. für Anilinfabrikation, German Patent 17,311, 1881; *J.S.C.I.*, 1882, 1, 226; Dobrzycki, *J. pr. Chem.*, 1887, (2) 36, 390.

[43d] A.-G. für Anilinfabrikation, German Patent 23,775, 1882; *J.S.C.I.*, 1884, 3, 105.

[43e] Meyer and Bernhauer, *Monatsh.*, 1929, 53 and 54, 721; *Chem. Abs.*, 1930, 24, 346.

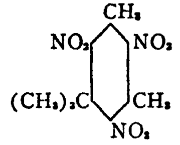
[43f] Hinsberg, German Patent 538,376, 1930; *Chem. Abs.*, 1932, 26, 1617.



has also been effected in the presence of alcoholic potassium hydroxide solution.[43h] Linner[43i] has proposed to conduct the reaction in this manner: Isobutylene is bubbled through a solution of phenol in carbon tetrachloride containing aluminum chloride in suspension and a small quantity of tertiary-butyl chloride. The reaction is instituted by the alkyl chloride and the hydrogen chloride liberated combines with the isobutylene to form additional alkyl chloride to continue the reaction.

Para-tertiary-butyl-phenol melts at 97.5° to 98° C. and boils at 236° to 238° C.; para-tertiary-amylphenol melts at 93° to 94° C. and boils at 265° to 267° C.

The discovery of synthetic materials possessing the odor of musk (and hence termed "artificial musk") was made by Baur,[44] who developed methods for the large-scale production of these synthetic perfumes. Many of them are nitrated aromatic hydrocarbons containing a tertiary alkyl substituent (usually tertiary butyl) such as trinitro-tertiary-butyltoluene, trinitro-tertiary-butylethylbenzene, and trinitro-tertiary-butyl-m-xylene, the last named substance possessing the configuration



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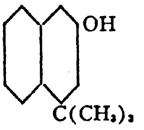
Not only hydrocarbons but nitrated phenols, aromatic ethers and ketones having a tertiary alkyl substituent were found to possess the characteristic musk-like odor. Among these may be mentioned dinitro-tertiary-butylacetophenone, trinitro-tertiary-butyl-m-cresol, and dinitro-tertiary-butylxylyl methyl ketone.[44a] The tertiary butyl group was introduced into these aromatic compounds by the Friedel-Crafts reaction, using tertiary butyl chloride. The products were then nitrated to yield the synthetic musks.

Some of the derivatives of the tertiary alkylated aromatic hydrocarbons, especially tertiary-butylbenzenesulphonic and tertiary-butylnaphthalenesulphonic acids, have been suggested as wetting, emulsifying, and foam-producing agents. 4-Tertiary-butyl-β-naphthol,



[43g] Gurewitsch, *Ber.*, 1899, **32**, 2428.

[43h] Lewis, *J.C.S.*, 1903, **83**, 329.

[43i] Austrian Patent 124,281, 1931; assigned to Soc. Reichhold, Flügger and Boecking; *Chem. Abs.*, 1932, **26**, 735; French Patent 697,711, 1930; *Chem. Abs.*, 1931, **25**, 3013.

[44] *Ber.*, 1891, **24**, 2832; *Compt. rend.*, 1890, **111**, 238; *Chem. Zentr.*, 1890, **2**, 431; German Patent 47,599, 1888; *Chem. Zentr.*, 1889, **2**, 720; British Patent 4963, 1889; *J.S.C.I.*, 1890, **9**, 545; these were followed by a series of patents and descriptions in various journals.

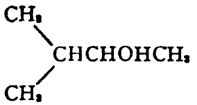
[44a] For a fuller account see Schotz, "Synthetic Organic Compounds," D. Van Nostrand Co., New York, 1925.

prepared by the action of tertiary butyl chloride on β-naphthol in the presence of aluminum chloride, has been proposed as a plasticizer for cellulose derivatives and as a dye component.[45]

HIGHER SECONDARY ALCOHOLS FROM PETROLEUM

The important higher secondary alcohols which may be manufactured from the volatile liquid olefins are secondary amyl and hexyl alcohols. Secondary heptyl and higher alcohols can be made if there is sufficient demand for them. Heretofore these alcohols have been exceedingly rare and difficult to prepare in any but small quantities. The higher secondary alcohols produced from the olefins of cracking gas and cracked gasoline consist largely of β alcohols, i.e., normal chain alcohols with a hydroxyl group attached to the second carbon atom. According to Johns,[46] laboratory researches (unpublished) indicate that all the secondary alcohols obtained are of this type. It is possible, however, that although the β alcohols may predominate, there may also be a smaller amount of secondary alcohols in which the hydroxyl group is attached to the third carbon atom of the chain. There is an increasing number of isomers even of the β alcohols as the number of carbon atoms in the molecule increases because branched chains may exist. For example, there are two β pentanols which have the following formulas:

$CH_3CH_2CH_2CHOHCH_3$
Methyl-n-propylcarbinol



$$\begin{matrix} CH_3 \\ \quad\searrow \\ \quad CHCHOHCH_3 \\ \quad\nearrow \\ CH_3 \end{matrix}$$

Methylisopropylcarbinol

The secondary alcohols shown in Table 88 are likely to occur in the products obtained by absorbing the higher olefins (from cracking gas or gasoline) in sulphuric acid and hydrolyzing.[47]

Secondary amyl alcohol (*pentanol-2*) has a hydrocarbon-like odor with a slight choking action in the bronchial tubes. It is less soluble in water than the lower secondary alcohols, dissolving in 6 volumes of water at ordinary temperatures. The product made from cracking gas probably contains some of the branched-chain isomer, methylisopropylcarbinol. It may find application in the lacquer industry in the form of its acetate, boiling point 135°-138° C., a mobile liquid with a peppery odor similar to that of turpentine. Park and Hopkins[48] examined a sample of secondary amyl acetate (containing 85 per cent of ester and 15 per cent of alcohol, and having a boiling range of 128° to 134° C., $d^{15.5}_{15.5}$ 0.863, n^{20}_{D} 1.4021). It was concluded that this and other secondary esters could safely be used either in the base lacquer or thinner. These secondary esters are made in the usual way by direct esterification in the presence of a mineral oil fraction of initial boiling point 300° C.[49]

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[45] Koenigsberger, U. S. Patent 1,788,529, Jan. 13, 1931; assigned to Dehls and Stein; *Chem. Abs.*, 1931, **25**, 974.

[46] *Ind. Eng. Chem.*, 1923, **15**, 448.

[47] Data from the following sources: Davis and Murray, *Ind. Eng. Chem.*, 1926, **18**, 844; Ullmann, "Enzyklopädie der technischen Chemie," Urban and Scharzenberg (Berlin); Beilstein, "Handbuch der organischen Chemie." Verlag von Julius Springer, Berlin, **1918**; Durrans, "Solvents," Chapman and Hall, London, **1930**; Brooks and Humphrey, *J.A.C.S.*, 1918, **40**, 822.

[48] *Ind. Eng. Chem.*, 1930, **22**, 826.

[49] Standard Oil Development Co., British Patent 305,308, 1927; *Brit. Chem. Abs.* **B**, 1929, 275. For similar application of the Friedel-Crafts reaction see Schaarschmidt, French Patent 42,410, 1933; *Chem. Abs.*, 1933, **27**, 4813; French Patent 735,786, 1931; *Chem. Abs.*, 1933, **27**, 991; British Patent 388,734, 1933; *Chem. Abs.*, 1933, **27**, 4538; Mark, Dunkel and Roell, U. S. Patent 1,899,582, Feb. 28, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2961; I. G. Farbenindustrie A.-G., British Patent 391,600, 1932; *Brit. Chem. Abs.* **B**, 1933, 777; Nenitzescu and Cantuniari, *Ber.*, 1932, **65B**, 807. See also von Braun, *Ber.*, 1931, **64B**, 2869.

TABLE 88.—*Constants of Some Secondary Alcohols.*

Alcohol	B.P. ° C. (760 mm.)	Density	Refractive Index	
Methyl-n-propylcarbinol .... (pentanol-2)	119°	d_{20}^{20} 0.810	n_D^{20} 1.4077	Acetate, b.p. 134° C.
Methylisopropylcarbinol .... (3-methylbutanol-2)	112.5°	d_4^{20} 0.833	—	—
Methyl-n-butylcarbinol .... (hexanol-2)	139°–140°	d_4^{20} 0.822	n_D^{20} 1.4193	Acetate, b.p. 153° C.
Methylisobutylcarbinol .... (4-methylpentanol-2)	130°	—	—	Acetate, b.p. 148° C.
Methyl-n-amylcarbinol[a] .... (heptanol-2)	158.7° (741 mm.) 66.7° (16.5 mm.)	d_4^{20} 0.817	n_D^{20} 1.4210	—

[a] Sherrill, *J.A.C.S.*, 1930, **52**, 1982.

Methylisopropylcarbinol is remarkable in that, on treatment with hydrogen halides, it is converted into the derivatives of methyldiethylcarbinol, a reaction explainable on the assumption that the intermediate formation of trimethylethylene first takes place.

Secondary hexyl acetate is likely to be of value in the lacquer industry.[50] A sample examined by Park and Hopkins had the following properties, 85 to 88 per cent ester, boiling range 146° to 156° C., $d_{15.5}^{15.5}$ 0.863, n_D^{20} 1.4081. It is a solvent for rosin, ester gum, dammar, kauri, cumar, pontianac, manila, elemi, asphalt, tars, and pitches, but not for shellac. Its solubility in water at 25° C. is less than 0.1 cc. per 100 cc. of water.

Secondary heptyl alcohol (*heptanol-2*) may be prepared synthetically by roundabout methods[51] but, if available in sufficient quantities, may find application in the lacquer industry (in the form of its esters[51a]) and for chemical synthesis.

All the secondary alcohols, amyl, hexyl, and heptyl included, may be converted into ketones, particularly by catalytic oxidation. For instance, Ottensooser[52] obtained an optimum yield of 79 per cent of the ketone from secondary octyl alcohol by oxidation with air in the vapor phase at 330° to 340° C. in the presence of a zinc oxide catalyst. In this way it should be possible to make large quantities of the higher ketones (which are excellent solvents for industrial purposes, particularly in cellulose acetate and nitrate lacquers) from the above secondary alcohols. Pentanol-2 would yield methyl propyl ketone and 3-methylbutanol-2, methyl isopropyl ketone. In general, methyl alkyl ketones could be produced from the higher β alcohols.

HIGHER TERTIARY ALCOHOLS FROM PETROLEUM

Formerly the higher tertiary alcohols were more or less chemical curiosities which had been produced only in relatively small quantities or not at all. The possibility of obtaining large amounts of these alcohols from the olefins of cracking gas and cracked gasoline has opened up a wide field for investigation, more especially as regards their application in industry. As far as is known, no outlet has been discovered which is capable of absorbing the large quantities of these materials which might be available. The unique chemical and physical properties of these alcohols, however, appear to render certain their ultimate large-scale utilization in industry either as special solvents and crystallizing media, in chemical syntheses, or for other purposes.

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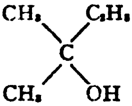
[50] Park and Hopkins, *Ind. Eng. Chem.*, 1930, **22**, 826.

[51] See Sherrill, *J.A.C.S.*, 1930, **52**, 1982. Whitmore and Otterbacher, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1930, 10, 60.

[51a] Van Schaack (U. S. Patent 1,815,878, July 21, 1931; assigned to Van Schaack Bros. Chem. Works, Inc.; *Brit. Chem. Abs.* **B**, 1933, 218) suggested as softeners for cellulose nitrate, the esters of higher secondary alcohols and dibasic acids such as 2-n-octyl succinate or phthalate.

[52] *Bull. soc. chim.*, 1927, (4) 41, 324; *Chem. Abs.*, 1927, **21**, 2089.

The general characteristics of the tertiary alcohols as a class have already been noted in discussing tertiary butyl alcohol, namely their unique physical properties including high melting point and low boiling point, the ease of replacement of the hydroxyl group by halogen acids (and even hypochlorous acid) to form esters, their ease of dehydration in the presence of even weak organic acids, their resistance to oxidation and stability to halogens, the impossibility of direct esterification by organic acids or acid chlorides and the extraordinary ease of hydrolysis of their esters.

Tertiary amyl alcohol (*dimethylethylcarbinol*)  is a liquid at ordinary temperatures, boiling point 101.8° C., melting point —12° C., d^{20}_{4} 0.8093, n^{20}_{D} 1.4052,[53] and possessing a camphoraceous odor. It is soluble in 8 volumes of water at ordinary temperatures. This alcohol is formed by the hydration of both trimethylethylene and unsymmetrical methylethylethylene. It is readily dehydrated, especially in acid solutions, to yield trimethylethylene. It is comparatively stable to bromine at room temperature but the solution rapidly decolorizes at 80° C. Tertiary amyl alcohol is said to be "a safe, rapidly acting, and occasionally useful but not analgesic hypnotic." [54]

Tertiary amyl chloride, which is prepared by the action of concentrated hydrochloric acid on the alcohol, is a liquid boiling at 86° C., which should be useful for introducing the tertiary amyl group into organic compounds. *Tertiary amyl hypochlorite,* made by passing chlorine into an alkaline solution of the alcohol at ordinary temperatures, is a mobile liquid of d^{25}_{4} 0.8547, boiling with decomposition at 76° C.[55]

The properties of the tertiary hexyl alcohols, of which three isomers exist, are very inadequately known. Davis and Murray [56] described two of these alcohols, namely a straight-chain tertiary hexyl alcohol (probably dimethyl-n-propylcarbinol), boiling point 123° C., d^{20}_{4} 0.824, and a branched-chain tertiary hexanol (probably dimethylisopropylcarbinol) of boiling point 117.6° C., and d^{20}_{4} 0.839.

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[53] Davis and Murray, *Ind. Eng. Chem.*, 1926, **18**, 844.
[54] U. S. Dispensatory, 20th Edition.
[55] Chattaway and Backeberg, *J.C.S.*, 1923, **123**, 2999.
[56] *Ind. Eng. Chem.*, 1926, **18**, 844.

Chapter 18

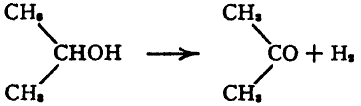
Production, Properties, and Uses of Ketones Derived from Secondary Alcohols and from Hydrocarbons

Ketones are derived from secondary alcohols made by the hydration of the lower olefins of cracking gas and represent an important use for these alcohols. As a class, ketones are among the most valuable solvents of commerce and find application in a number of industries. Acetone, particularly, is one of the most widely used of low-boiling solvents. In addition to being solvents for a large number of organic substances, the ketones also undergo condensation reactions and are thus of significance in organic chemical synthesis.

Although acetone and the higher ketones are still mainly produced from raw materials other than petroleum (for example by fermentation of grain or by wood distillation), the petroleum hydrocarbons offer great possibilities as suitable raw materials for the manufacture of these solvents. The oxidation or direct dehydrogenation of secondary alcohols, made from the lower olefinic hydrocarbons of cracking gas and cracked gasoline, readily yields ketones.[1] It has also been demonstrated that ketones may be synthesized directly from the lower paraffins by the Friedel-Crafts reaction.

PRODUCTION OF ACETONE

Formerly, acetone was principally produced by the destructive distillation of wood, but the greater part of the acetone now available, together with normal butanol, is made by the fermentation of carbohydrate material by the Fernbach-Strange-Weizmann process.[2] Although this method is economical, isopropyl alcohol (derived from the propylene of cracking gas) has been the subject of many investigations directed to its conversion to acetone.[3] The usual methods for the production of acetone in this manner involve either catalytic oxidation of isopropyl alcohol with air or its dehydrogenation by passage (without air) over a heated catalyst. Both these procedures result in the removal of hydrogen:



When oxidation is employed, the hydrogen is, of course, removed in the form of water. Sabatier and Senderens[4] have shown that metallic copper is an excellent dehydrogenating catalyst for primary and secondary alcohols. In the presence of this catalyst, isopropyl alcohol is slowly dehydrogenated to acetone at 150° C., and rapidly and smoothly at all temperatures between 250° and 430° C. without the formation of large amounts of propylene. With many contact substances, dehydration, leading to the formation of propylene, occurs. Many processes have been developed to better the performance of the copper catalyst of Sabatier and Senderens. Metallic sulphides have been recommended,[5] and the phosphides, selenides, tellurides, antimonides, arsenides, and the bismuthates of zinc, cadmium, nickel, cobalt, iron, aluminum, calcium, and magnesium have been suggested[6] as catalysts for the dehydrogenation of alcohols to ketones and aldehydes. Dehydrogenation of isopropyl alcohol to acetone and hydrogen by contact with lead at 625° C. is the basis of another process.[7] Molten lead can be replaced by molten alloys or salts, e.g., an equimolecular mixture of barium and calcium chlorides, or equal parts of potassium and sodium chlorides. Chaffette[7a] suggested halides, oxides, carbonates, phosphates, acetates, stannates, arsenates, antimonates, molybdates, vanadates, and borates of the metals of the second, seventh and eighth groups as catalysts for the production of acetone from alcohols and steam.

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[1] Ellis and Wells, U. S. Patent 1,450,493, Apr. 3, 1923; see Chapter 36.

[2] British Patent 21,073, 1912; *J.S.C.I.*, 1913, **32**, 987. British Patent 4,845, 1915; *J.S.C.I.*, 1919, **38**, 301A.

[3] Ellis and Wells, *loc. cit.* Baldwin (*J.S.C.I.*, 1930, **49**, 53T, *Ind. Eng. Chem., News Ed.*, 1930, **8** (2), 12.) reported considerable quantities of acetone were being made in the United States from propylene of petroleum origin.

[4] *Ann. chim. phys.*, 1905, (8) **4**, 463, 467.

The dehydrogenation of primary, secondary and tertiary alcohols by catalytic oxidation has been the subject of a number of important researches.

Ipatiev[8] investigated the catalytic oxidation of isopropyl alcohol to acetone at 200° to 230° C. and of secondary butyl alcohol at higher temperatures, using nickel. Trillat[9] investigated the catalytic transformation of isopropyl, isobutyl, isoamyl, and iso-octyl alcohol into the corresponding ketones, using a platinum wire gauze. He also extended his experiments to include tertiary butyl and amyl alcohols which yielded acetone and some formaldehyde. Sabatier and Senderens[10] also studied the catalytic oxidation of secondary and tertiary alcohols by different metals. Isopropyl, isobutyl, and iso-octyl alcohols gave the corresponding ketones in good yields, when copper, nickel, cobalt and platinum were used as catalysts. Gibbs[11] described the production of acetone by catalytic oxidation of isopropyl alcohol, made from the waste gases of the Burton cracking process. Lang[12] developed a method for producing ketones (or aldehydes) in which manganic salts at high temperatures were the catalysts, and Williams and White[13] suggested passing alcohol vapors over brass heated to 500° to 800° C.

Still another procedure consists in conducting isopropyl alcohol vapors and air (the quantity of air being such that the proportion of oxygen in the mixture is just equal to, or slightly less than, that actually required) over metallic catalysts, e.g., copper or copper alloys, at 475° to 800° C. The yield of acetone may be as high as 75 per cent of the theoretical.[14]

Moureu and Mignonac[15] investigated the catalytic oxidation of various alcohols in the vapor state in the presence of finely divided silver (deposited on asbestos by precipitation from silver nitrate solution with formaldehyde) at 230° to 300° C. Intense local heating made it preferable to conduct the operation in two stages, i.e., first to pass the alcohol vapor mixed with 40 to 50 per cent of the requisite amount of air over the catalyst, and then to mix the issuing vapors with a further 50 per cent of air and pass the new mixture over a second catalyst. Excellent results were reported with isopropyl alcohol. This method was subsequently modified[16] in that the mixture of alcohol vapor and air was passed at a reduced pressure (20 to 40 mm.) over a catalyst of finely divided silver at 230° to 300° C. Later, Ottensooser[17] by the vapor-phase oxidation of isopropyl alcohol with air (in the presence of a zinc oxide catalyst prepared from ammonium zincate[18]) obtained an 84.5 per cent conversion of this alcohol into acetone, the optimum temperature being 315° to 325° C. Acetone can be produced by subjecting ethyl alcohol vapor diluted with an inert gas to the action of catalysts at 250° to 650° C.[19]

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[5] I. G. Farbenindustrie A.-G., British Patent 262,120, 1927; *Brit. Chem. Abs.* **B**, 1927, 541.

[6] I. G. Farbenindustrie A.-G., British Patent 263,877, 1927; *Brit. Chem. Abs.* **B**, 1927, 669.

[7] Bataafsche Petroleum Maatschappij, British Patent 339,491, 1929; *Chem. Abs.*, 1931, **25**, 2440; French Patent 706,731, 1931; *Chem. Abs.*, 1932, **26**, 1296; German Patent 552,985, 1930; *Chem. Abs.*, 1932, **26**, 5578. The dehydrogenation of isopropyl alcohol can also be effected at 120° to 300° C. in the presence of powdered nickel, cobalt or copper, see Rheinische Kampfer Fabrik, British Patent 347,931, 1930; *Brit. Chem. Abs.* **B**, 1931, 834. See also Al, U. S. Patent 1,883,443, Oct. 18, 1932; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 1013.

[7a] French Patents 730,797 and 730,798, 1932; *Chem. Abs.*, 1933, **27**, 306.

[8] *Ber.*, 1907, **40**, 1276.

[9] *Compt. rend.*, 1901, **132**, 1495; *Chem. Soc. Abs.*, 1901, **80** (1), 496.

[10] *Compt. rend.*, 1903, **136**, 983; *Chem. Soc. Abs.*, 1903, **84** ((1), 454.

[11] *Chem. Met. Eng.*, 1920, **22**, 407.

[12] German Patent 166,357, 1906; *Chem. Zentr.*, 1906, **1**,. 1065.

[13] U. S. Patent 1,460,876, July 3, 1923; *J.S.C.I.*, 1923, **42**, 952A. See also Bataafsche Petroleum Maatschappij, French Patent 729,742, 1932; *Chem. Abs.*, 1933, **27**, 306; British Patent 392,625, 1932; *Brit. Chem. Abs.* **B**, 1933, 776.

[14] Hunt, British Patent 173,539, 1921; *J.S.C.I.*, 1923, **42**, 30A.

[15] *Compt. rend.*, 1920, **170**, 258.

The effect of the physical and chemical nature of the catalyst material on the course of the oxidation of various alcohols in the vapor phase was investigated by Simington and Adkins.[20] The catalysts included copper, silver, platinum, nickel, alloys of copper with silver, zinc, bismuth, cadmium and palladium. Gauze, pellets, strip and wire catalysts were equally efficacious. The maximum yield of acetone from isopropyl alcohol, corresponding to a 76.1 per cent conversion, was obtained when using a catalyst of silver pellets.

Other catalysts that have been proposed include the following: a metal vanadate (excluding a simple alkali vanadate),[21] a gauze of zinc-copper alloy,[22] and metallic copper, iron, nickel, silver, platinum or the oxides of tin, chromium, cobalt or vanadium.[23] In general the mixture of air and alcohol in the proportions required (or with slightly less air than is actually necessary) is passed over the catalyst heated initially to about 500° C. The heat of reaction is sufficient to maintain the catalyst at the required temperature. Wells[24] has described certain catalysts, such as manganese dioxide or barium peroxide, to be used at somewhat lower temperatures, i.e., 100° to 250° C.

The catalytic oxidation of isopropyl alcohol to acetone is said to take place readily at 400° C. in the presence of copper, manganese dioxide, barium peroxide, a platinum metal, zinc oxide, cadmium oxide, uranium oxide, blue tungsten oxide, vanadium pentoxide, magnesia, beryllia, or zirconia to which has been added about 1 per cent of thorium oxide, cerium oxide, or other oxides.[25]

Other methods for the manufacture of acetone utilize acetic acid, ethyl alcohol, or acetylene as raw materials. The older method of converting acetic acid into acetone, so largely employed in the wood-distillation industry, consisted in the dry distillation of the calcium salt of that acid. According to Ardagh, Barbour, McClellan and McBride,[26] the optimum distillation temperature is 430°

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[16] *Compt. rend.*, 1920, 171, 652.

[17] *Bull. soc. chim.*, 1927, (4) 41, 324; *Chem. Abs.*, 1927, **21**, 2089.

[18] *Cf.* Lazier and Adkins, *J.A.C.S.*, 1925, 47, 1719.

[19] Bloomfield, Swallen and Crawford, Canadian Patent 321,646, 1932; assigned to Commercial Solvents Corp.; *Chem. Abs.*, 1932, **26**, 3265.

[20] *J.A.C.S.*, 1928, 50, 1449.

[21] Maxted and Coke, British Patent 238,033, 1925; *Chem. Abs.*, 1926, **20**, 1814.

[22] Williams and Haller, U. S. Patent 1,450,569, Apr. 3, 1923; *Chem. Abs.*, 1923, 17, 2428. Williams and White, U. S. Patent 1,460,876, July 3, 1923; *Chem. Abs.*, 1923, 17, 2887.

[23] Wells, U. S. Patent 1,497,817, June 17, 1924; *Chem. Abs.*, 1924, **18**, 3194.

[24] U. S. Patent 1,541,545, June 9, 1925; *Chem. Abs.*, 1925, **19**, 2210.

[25] Bataafsche Petroleum Maatschappij; British Patent 337,566, 1929; *Brit. Chem. Abs.* **B**, 1931, 194. Dutch Patent 29,252, 1933; *Chem. Abs.*, 1933, **27**, 3225; German Patent 564,210, 1930; *Chem. Abs.*, 1933, **27**, 1013; Dutch Patent 28,606, 1932; *Chem. Abs.*, 1933, **27**, 1359; French Patent 703,511, 1931; *Chem. Abs.*, 1931, **25**, 4286.

[26] *Ind. Eng. Chem.*, 1924, **16**, 1133.

to 440° C. This procedure, however, now has to compete with the direct catalytic production from acetic acid which takes place according to the reaction,

$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$

The reaction is complicated by the simultaneous occurrence of the decomposition of acetic acid to methane,

$$CH_3COOH \longrightarrow CO_2 + CH_4$$

a breakdown which may be reduced by the choice of proper catalysts and operating conditions.[27] A large number of catalysts for the direct synthesis of acetone from acetic acid in the vapor phase has been proposed, among which may be mentioned the following: thorium and uranium oxides,[28] copper at 390° to 410° C.,[29] zinc oxide at 400° C. and zinc turnings at 250° to 280° C.,[30] manganese salts at 450° C.,[31] manganese dioxide at 350° to 450° C.,[32] oxides, hydroxides or acetates of calcium and barium precipitated on aluminum and used at 300° to 400° C.[33] During the World War a commercial process was developed by the Canadian Electro-Products Co. which consisted in passing acetic acid vapor over cast iron balls coated with lime or baryta or a mixture of these with bases such as magnesia. The operating temperature was 485° C. and the yield of acetone was said to be 95 per cent of the theoretical, based on the acid consumed.[34]

Another method of producing acetone depends upon the catalytic treatment of ethanol with steam at high temperatures.[35] The reaction (which yields very pure acetone together with hydrogen and carbon dioxide) may be represented:

$$2CH_3CH_2OH + H_2O \longrightarrow CH_3COCH_3 + 4H_2 + CO_2$$

Probably it involves several intermediate steps, including the possible formation of acetic acid.[35a]

Donath[36] investigated the oxidation of ethyl alcohol to acetone at high temperatures in the presence of the higher oxides of manganese, and Roka[37] examined the production of acetone by heating a mixture of ethyl alcohol and water vapors at 250° to 650° C. in the presence of oxygen-containing catalysts of iron, manganese, copper and calcium or magnesium.

Oxley, Groombridge and Thomas[38] proposed the use of catalysts consisting of

[27] Squibb, *J.A.C.S.*, 1895, **17**, 187; 1896, **18**, 231.

[28] Senderens, *Bull. soc. chim.*, 1909, (4) **5**, 905, 916.

[29] Sabatier and Senderens, *Ann. chim. phys.*, 1905, (8) **4**, 476. *Cf.* Querfurth, German Patent 533,851, 1929; assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1932, **26**, 735; Holzverkohlungs-Industrie, French Patent 38,656, 1930; *Chem. Abs.*, 1932, **26**, 2752; Chaffette, French Patent 743,764, 1933; *Chem. Abs.*, 1933, **27**, 3951; Sandkuhl, U. S. Patent 1,892,011, Dec. 27, 1932; *Chem. Abs.*, 1933, **27**, 1891; French Patent 696,658, 1930; *Chem. Abs.*, 1931, **25**, 2734; both assigned to Rheinische Kampfer-Fabrik G.m.b.H.

[30] Mailhe, *Bull. soc. chim.*, 1909, (4) **5**, 618, 620.

[31] Pascal, *Mém. poud.*, 1926, **22**, 1; *Chem. Abs.*, 1927, **21**, 563.

[32] Soc. anon. des Acieries et Forges de Firminy, British Patent 134,144, 1919; *Chem. Abs.*, 1920, **14**, 746.

[33] Stockholms Superfosfat Fabriks Akt., British Patent 171,391, 1921; *J.S.C.I.*, 1922, **41**, 786A. Soc. Pagès Camus et Cie., German Patents 214,151 and 214,152, 1909; *Chem. Zentr.*, 1909, **2**, 1395.

[34] *Canadian Chem. J.*, 1919, **3**, 56; *Chem. Abs.*, 1919, **13**, 958. Matheson, British Patent 138,679, 1919; *J.S.C.I.*, 1920, **39**, 312A.

[35] Holzverkohlungs-Industrie A.-G., British Patent 347,593, 1930; *Brit. Chem. Abs.* **B**, 1931, 753; British Patent 359,430, 1931; *Brit. Chem. Abs.* **B**, 1932, 172. Dreyfus, British Patent 338,518. 1929; *Chem. Abs.*, 1931, **25**, 2437; French Patent 698,858, 1930; *Chem. Abs.*, 1931, **25**, 3358.

[35a] Dreyfus (British Patent 345,271, 1929; *Chem. Abs.*, 1932, **26**, 156) reacts ethyl alcohol with barium hydroxide at a high temperature to produce barium acetate and obtains acetone from this by further heating.

[36] *Chem.-Ztg.*, 1888, **12**, 1191; *Chem. Soc. Abs.*, 1889, **56**, 230. *Chem.-Ztg.*, 1927, **51**, 924; *Brit. Chem. Abs.* **B**, 1928, 150.

[37] U. S. Patent 1,663,350, Mar. 20, 1928; *Chem. Abs.*, 1928, **22**, 1596; German Patent 475,428, 1924; *Chem. Abs.*, 1929, **23**, 3234; both patents assigned to Holzverkohlungs-Industrie A.-G.

[38] British Patent 353,467, 1930; assigned to British Celanese Co., Ltd.; *Brit. Chem. Abs.* **B**, 1931, 1132.

an alkaline-earth oxide together with a weak acidic oxide, such as aluminum or zinc oxide, for the conversion of ethylene, aliphatic alcohols, aldehydes or esters by steam into aliphatic ketones. For example, a 60 to 70 per cent yield of acetone is stated to be obtained from steam and ethyl alcohol with a calcium oxide-zinc oxide "cement" catalyst at 465° to 480° C.

The preparation of acetone from acetylene is accomplished by treatment of a mixture of that hydrocarbon with steam under the influence of certain catalysts at relatively high temperatures. The acetone so obtained is usually accompanied by other products. The following materials are suggested as catalysts for the process: iron oxide,[39] thorium oxide or a double compound of thorium with alkali or alkaline-earth metals,[40] such as the double thorium-potassium carbonate $K_6Th(CO_3)_5$. The reaction temperature specified is about 450° C. and the conversion is usually not more than 40 per cent of the theoretical. According to the Holzverkohlungs-Industrie A.-G.,[41] the exothermic production of acetone from acetylene and steam at elevated temperatures is conveniently carried out along with the endothermic production of acetone from aliphatic alcohols of two or more carbon atoms per molecule. The raw material may be residual acetylene (containing uncondensed acetaldehyde, water, and acetic acid) obtained in the production of acetaldehyde from acetylene. Catalysts include the oxides of iron, zinc, or nickel with promoters such as alumina, barium carbonate, lime, or magnesia. Conversion of acetylene and excess steam into acetone at 275° to 725° C. in the presence of a composite catalyst of zinc chloride, iron and chromium oxides has also been described.[41a] Baur [41b] prepared ketones and aldehydes (propionaldehyde and acetone) by passing vapors of 1,2-oxides of hydrocarbons containing 2 to 4 carbon atoms at temperatures of 200° to 450° C. over a catalyst consisting of a halide of an alkaline earth metal. Lazier [42] used a mixture of a secondary alcohol and phenol to prepare acetone (mixed with cyclohexanol and cyclohexanone). The mixture was heated to 200° C. at a pressure of 500 pounds per square inch in the presence of a nickel catalyst.

Döderlein [42a] obtained acetone from oil resulting from the dry distillation of bituminous shale. After refining the oil with sulphuric acid the sludge was diluted with water and distilled. The ketones were recovered from the distillate.

PROPERTIES OF ACETONE

Acetone is a colorless mobile liquid having the following physical constants: b.p. 56.5° C.; m.p. —94.9° C.; d_4^0 0.81378; d_4^{15} 0.79705; d_4^{30} 0.77986; critical temperature 234.4° C.; latent heat of vaporization 125.28 Cals. per kgm. at 56.3° C. It is miscible in all proportions with water, alcohol, ether, many esters, and with many mineral and vegetable oils. It can be salted out of its aqueous solutions by calcium chloride. It is one of the most powerful solvents known and readily dissolves cellulose acetate, benzoate, nitrate and acetonitrate, ethyl cellulose, and many resins including glyceryl phthalate resins, crotonaldehyde resins, benzyl abietate, vinyl resin, elemi, rosin, ester gum, and copal. It only partly dissolves shellac, mastic, hard copals, and montan wax. Its solvent action on pitches and rubbers varies widely with the character of those products. A considerable number of azeotropic mixtures with other organic liquids are known, including one with methanol (13.5 per cent of methanol) boiling at 55.95° C., and one with chloroform (80 per cent chloroform) boiling at 64.7° C. The latter is remarkable in possessing a higher boiling point than either of its components.[43]

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[39] Holzverkohlungs-Industrie A.-G., British Patent 347,695, 1930; *Brit. Chem. Abs.* **B**, 1931, 753. See also Meerwein and Morschel, U. S. Patent 1,865,940, July 5, 1932; assigned to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1932, **26**, 4347; I. G. Farbenindustrie A.-G., British Patent 391,600, 1933; *Chem. Abs.*, 1933, **27**, 5085; Bataafsche Petroleum Maatschappij, German Patent 552,985, 1930; *Chem. Abs.*, 1932, **26**, 5578; French Patent 706,731, 1930; *Chem. Abs.*, 1932, **26**, 1296; British Celanese, Ltd., British Patent 355,362, 1930; *Chem. Age (London)*, 1931, **25**, 525; Walter and Schulz, U. S. Patent 1,892,742, Jan. 3, 1933; assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1933, **27**, 2163.

[40] Elektrizitätwerk Lonza, British Patent 192,392, 1923; *J.S.C.I.*, 1923, **42**, 862A.

[41] British Patent 344,449, 1929; *Brit. Chem. Abs.* **B**, 1931, 620. *Cf.* Róka, U. S. Patent 1,821,324, Sept. 1, 1931; *Brit. Chem. Abs.* **B**, 1933, 217; German Patent 544,778, 1925; *Chem. Abs.*, 1932, **26**, 3515; both patents assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; Yamada, *J. Soc. Chem. Ind. Japan*, 1933, **36**, 193; *Brit. Chem. Abs.* **A**, 1933, 937.

[41a] Martin and Krchma, U. S. Patent 1,779,676, Oct. 28, 1930; assigned to Commercial Solvents Corp.; *Brit. Chem. Abs.* **B**, 1931, 666.

[41b] U. S. Patent 1,906,833, May 2, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3482. See also German Patent 528,822, 1929; *Chem. Abs.*, 1931, **25**, 5175; German Patent 535,651, 1930; *Chem. Abs.*, 1932, **26**, 994; British Patent 331,185, 1929; *Chem. Abs.*, 1931, **25**, 115; all patents assigned to I. G. Farbenindustrie A.-G.

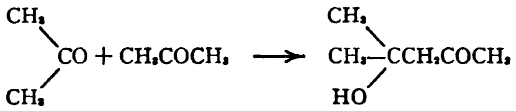
[42] U. S. Patent 1,829,869, Nov. 3, 1931; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1932, **26**, 788.

[42a] German Patent 571,226, 1930; *Chem. Abs.*, 1933, **27**, 2800; British Patent 376,862, 1932; *Chem. Abs.*, 1933, **27**, 4071.

In chemical properties, acetone exhibits a high order of reactivity with many organic and inorganic substances. Only a few of the more important reactions will be discussed.

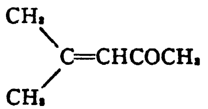
Iodine, chlorine, and bromine readily react with acetone in alkaline solution to form iodoform, chloroform, and bromoform, respectively, a reaction used for the manufacture of the two former materials.

When subjected to the action of alkalies acetone undergoes a condensation, very closely allied to the aldol condensation of aldehydes, which results in the formation of diacetone alcohol.[44]

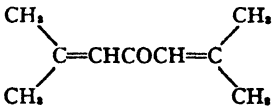


Diacetone alcohol

Under the influence of dehydrating agents, diacetone alcohol loses the elements of water with the production of mesityl oxide.



This latter substance may be prepared directly from acetone by the action of anhydrous alkalies, such as lime (CaO), or other reconstituting agents, e.g., zinc chloride or hydrogen chloride.[44a] The condensation may even proceed a stage further to yield phorone.



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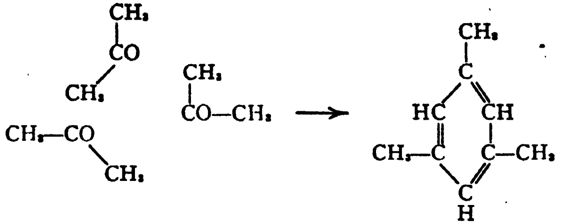
[43] Park and Hofmann, *Ind. Eng. Chem.*, 1932, 24, 132; see also Durrans, "Solvents," Chapman and Hall, Ltd., London, 1930.

[44] See Conant and Tuttle, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, 1, 45.

[44a] For the preparation of mesityl oxide see also Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, British Patent 383,474, 1932; *Chem. Abs.*, 1933, 27, 4253; Guinot, U. S. Patents 1,913,158 and 1,913,159, June 6, 1933; *Chem. Abs.*, 1933, 27, 4253; German Patent 559,738, 1930; *Chem. Abs.*, 1933, 27, 736.

By heating acetone under pressure at 300° to 320° C. in the presence of zinc chloride, Ipatiev, Petrov and Ivanov[44b] obtained a mixture of unsaturated hydrocarbons, of which a large proportion was diisobutylene. Mesityl oxide and isophorone were also found in the products.

In the presence of concentrated sulphuric acid, three molecules of acetone unite to form a cyclic compound, mesitylene.



Both mesityl oxide and diacetone alcohol are of some industrial importance. *Diacetone alcohol,* an odorless, colorless liquid, may be used as a solvent for cellulose acetate in lacquers, since it yields films having a brilliant gloss. The fact that it rather easily hydrolyzes to acetone (a more volatile liquid) mitigates against its general use in the preparation of lacquers. It is also a solvent for cellulose nitrate, and for many resins, including the copals. It is considered non-toxic.

Diacetone alcohol can be made by treating acetone in alcoholic solution with sufficient alkali (sodium hydroxide) to give a reaction with cresol red but not with o-cresolphthalein.[45] Conant and Tuttle[46] obtained diacetone alcohol in yields of 71 per cent of the theoretical by boiling acetone with barium hydroxide. Calcium hydroxide,[47] concentrated sodium or potassium hydroxide solutions,[48] and magnesium amalgam[49] have also been recommended for this preparation. Ellis[50] treated acetone with about 0.01 to 0.02 per cent of alkali metal hydroxide at a temperature below 30° C., and Thomson[51] used a suspension of potassium hydroxide in acetone and benzene at room temperature. Nitriles, such as hydroxyalkylaminonitriles, can be prepared by the reaction of hydrocyanic acid on a mixture of a ketone and hydroxyalkylamines.[51a]

Mesityl oxide, a liquid of strong odor and b.p. 129.5° C., is insoluble in water. It is an excellent solvent for cellulose acetate and nitrate and would probably find extensive application in the lacquer industry but for its rather objectionable odor. Mesityl oxide may be condensed with aliphatic alcohols to yield ethers of diacetone alcohol.[52]

[44b] *Ber.*, 1930, **63**, 2806; *J. Russ. Phys.-Chem. Soc.*, 1930, **12**, 1489; *Brit. Chem. Abs.* **B**, 1930, 1553.

[45] Usines de Melle, British Patent 356,609, 1930; *Brit. Chem. Abs.* **B**, 1932, 95.

[46] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, 1, 45; *Chem. Abs.*, 1926, **20**, 44. *Cf.* Kyriakides, *J.A.C.S.*, 1914, **36**, 534.

[47] Hoffman, *J.A.C.S.*, 1909, **31**, 722; German Patent 229, 678, 1909; *Chem. Zentr.*, 1911, 1, 275; U. S. Patent 1,082,424, Dec. 23, 1913; *Chem. Abs.*, 1914, **8**, 788. *Cf.* Clement, French Patent 505,073, 1917. Hoffman employed a modified Soxhlet extraction apparatus in which the condensed acetone vapors filtered through a heated granular mass of calcium hydroxide. Although only a small proportion of the acetone was converted to diacetone alcohol during each passage through the alkali, this procedure resulted in the concentrating of the alcohol in the residual liquid.

[48] Heintz, *Ann.*, 1873, **169**, 114. Koelichen, *Z. physik. Chem.*, 1900, **33**, 130.

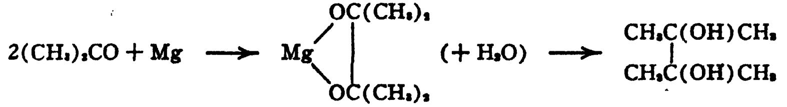
[49] Bouveault and Locquin, *Ann. chim. phys.*, 1910, (8) **21**, 411.

[50] U. S. Patent 1,701,473, Feb. 5, 1929; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1929, **23**, 1419. See also Lougovoy, U. S. Patents 1,844,430 and 1,844,431, Feb. 9, 1932; assigned to Ellis-Foster Co.; *Brit. Chem. Abs.* **B**, 1933, 296.

[51] U. S. Patent 1,654,103, Dec. 27, 1927; assigned to E. I. duPont de Nemours and Co., Inc. See also British Patents 308,285, 1927; assigned to Nobel Industries, Ltd.; *Chem. Abs.*, 1930, **24**, 127.

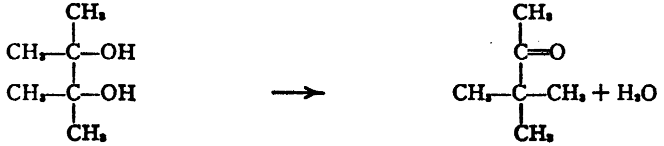
[51a] I. G. Farbenindustrie A.-G., British Patent 388,874, 1931; *Brit. Chem. Abs.* **B**, 1933, 457; British Patent 359,262, 1930; *Brit. Chem. Abs.* **B**, 1932, 173. See also Dreyfus, French Patent 715,030, 1931; *Chem. Abs.*, 1932, **26**, 1617.

In addition to undergoing condensation of the aldol type, acetone may also yield pinacol.[53] This is accomplished by allowing acetone to react with magnesium amalgam, and then hydrolyzing the product. The reactions may be represented by



Distillation of the dry magnesium compound in a current of carbon dioxide gives pinacoline, acetone, isopropyl alcohol and mesityl oxide.

A further important step in this condensation, and one that is frequently used in organic synthesis, is the transformation of pinacol into pinacoline by mineral acids.



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ C{=}O \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array} + H_2O$$

Pinacol *Pinacoline*

Passage of acetone vapors over red-hot magnesium yields a solid black mass, which on the addition of water gives hydrogen and allylene (methylacetylene).[54]

Another interesting condensation is that of olefins with acetone to yield high molecular weight ketones. This takes place best at high pressures (1000 to 3000 pounds) at temperatures of 250° to 350° C. in the presence of oxide catalysts such as those of nickel, zinc, chromium and vanadium.[55] Metallic chlorides such as zinc chloride or ferric chloride may be used as promoters. Ethylene and acetone, for example, at 1000 pounds pressure and 450° to 500° C. give propyl methyl ketone, and propylene and acetone at 2000 pounds pressure and 300° to 350° C. form butyl methyl ketone.

USES OF ACETONE

Two of the more important applications of acetone are in the manufacture of smokeless powder and celluloid. Acetone is used in making both cellulose acetate and nitrate solutions and in the production of certain kinds of artificial silk. Its solvent properties are utilized in the extraction or purification of a large number of organic products, such as fats and resins, and for numerous other purposes such, for example, as the scouring of wool. A solvent made by blending acetone with aromatic hydrocarbons, e.g., benzene or toluene, has been suggested as a dewaxing medium for lubricating oils.[56] The property of acetone as a solvent for acetylene is utilized on a large scale for the storing of that gas in steel cylinders for welding purposes. Acetylene is absorbed by a mixture of acetone and a porous earth and, in this form, can be safely handled even under considerable pressures, whereas acetylene normally explodes violently when compressed to a few atmospheres pressure. Acetone has been proposed in admixture with other liquids as a fuel for internal-combustion engines.[57] A mixture of acetone cyanohydrin and ethylene chloride in equal portions has been suggested as an insecticide.[57a]

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[52] Simms, U. S. Patent 1,823,704, Sept. 15, 1931; assigned to Commercial Solvents Corp.; *Chem. Abs.*, 1932, **26**, 152.

[53] Couturier and Meunier, *Compt. rend.*, 1905, **140**, 721; *Chem. Soc. Abs.*, 1905, **88** (1), 326.

[54] Keiser, *Amer. Chem. J.*, 1896, **18**, 328; *Chem. Soc. Abs.*, 1896, **70** (1), 457.

[55] Brown, U. S. Patent 1,757,830, May 6, 1930; assigned to Commercial Solvents Corp.; *Chem. Abs.*, 1930, **24**, 3247.

[56] Indian Refining Co., French Patent 741,633, 1932; *Chem. Abs.*, 1933, **27**, 2800; French Patents 734,254 and 734,797, 1932; *Chem. Abs.*, 1933, **27**, 1161. The Texas Co., French Patent 734,402, 1932; *Chem. Abs.*, 1933, **27**, 1161. See also Nottage (*J. Inst. Pet. Tech.*, 1932, **18**, 943; *Chem. Abs.*, 1933, **27**, 1494) for a description of the fractionation of lubricating oils with acetone. See also Anderson, U. S. Patent 1,907,703, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3813; Texaco Development

Acetone is also the raw material for the manufacture of a number of synthetic organic chemicals, among which may be mentioned the drug, sulphonal, and the perfume, ionone, and it has been employed in the synthesis of indigo. Organic acid anhydrides have been prepared by treating organic acids and ketones, for example, acetic acid and acetone, at temperatures of about 600° C.[57b]

Duprat[57c] obtained several complex compounds of ferrocyanic and ferricyanic acid with ketones and aldehydes. The ferricyanic complexes decomposed when dried *in vacuo* over sulphuric acid, but ferrocyanic complexes could be purified and their exact composition determined.

The hydrogenation of acetone to isopropyl alcohol may be effected either by passing acetone and hydrogen over a catalyst at atmospheric or increased pressures or by conducting the hydrogenation in the liquid phase, i.e., by introducing hydrogen under pressure into a suspension of the catalyst in liquid acetone. Sabatier and Senderens[58] obtained an 85 per cent yield of isopropyl alcohol from acetone by hydrogenation over a nickel catalyst at 115° to 125° C. and observed that the reaction is very slow. Maxted[59] secured rapid hydrogenation to isopropyl alcohol by distilling acetone in a current of hydrogen at 100 atmospheres over a granulated nickel catalyst. For good yields a circulation method is desirable and the hydrogen should be in excess. Ipatiev's method of hydrogenation gives excellent yields of acetone at 100 to 200 atmospheres pressure in the presence of a nickel catalyst at 210° to 220° C. (at higher temperatures decomposition ensues). With a copper catalyst, higher temperatures (280° to 300° C.) are necessary to give a 65 per cent yield of acetone.[60] The usual industrial method of hydrogenation is to agitate acetone, carefully freed from catalyst poisons, with hydrogen under pressure in the presence of a nickel catalyst. Senderens and Aboulenc[61] found that the hydrogenation proceeded smoothly at 110° C. and 30 atmospheres in the presence of a nickel suboxide catalyst. Platinum black has also been used successfully as a catalyst.[62] The industrial method is further exemplified by Riedel,[63] who conducted the hydrogenation of acetone in the liquid phase at 100° C. and 15 atmospheres hydrogen pressure in the presence of a catalyst consisting of the mixed carbonates of nickel, cobalt, and copper in the molecular proportions, 60:30:10.

According to Adkins and Connor,[64] copper chromite is a very active catalyst

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Corp., French Patent 738,953, 1932; *Chem. Abs.*, 1933, **27**, 2029; Langworthy, Canadian Patent 334,198, 1933; assigned to The Texaco Development Corp.; *Chem. Abs.*, 1933, **27**, 4918; Gouers, U. S. Patent 1,920,125, July 25, 1933; assigned to Indian Refining Co.; *Chem. Abs.*, 1933, **27**, 4919.

[57] Remler, *Chem. Met. Eng.*, 1923, **29**, 230. Terry, British Patent 230,354, 1924; *J.S.C.I.*, 1925, 491B.

[57a] Kono, Japanese Patent 94,739, 1932; assigned to Sankyo K. K.; *Chem. Abs.*, 1933, **27**, 1980.

[57b] Bataafsche Petroleum Maatschappij, British Patent 338,507, 1929; *Brit. Chem. Abs.* **B**, 1931, 237; French Patent 701,145, 1930; *Chem. Abs.*, 1931, **25**, 3670.

[57c] *Bull. inst. pin.*, 1933, **17**, 36; *Chem. Abs.*, 1933, **27**, 2674.

[58] *Compt. rend.*, 1903, **137**, 302.

[59] *J.S.C.I.*, 1926, **45**, 366.

[60] *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 75; *ibid.*, 1907, **39**, 681; *Chem. Abs.*, 1907, **1**, 2877; *Ber.*, 1907, **40**, 1270.

[61] *Bull. soc. chim.*, 1915, (4) **17**, 14.

[62] Vavon, *Compt. rend.*, 1912, **155**, 286.

[63] German Patent 444,665, 1919; *Brit. Chem. Abs.* **B**, 1928, 225.

[64] *J.A.C.S.*, 1931, **53**, 1091.

for the hydrogenation of organic substances. With this material, acetone is completely hydrogenated to isopropyl alcohol in the liquid phase at 150° C. under 100 to 150 atmospheres of hydrogen. For vapor-phase hydrogenation of acetone, Horsley[65] described a catalyst consisting of copper and silver with at least one oxide or hydroxide of a divalent metal. An alternative catalyst consists of a mixture of copper and nickel.[66]

Kirchov and Stepanov[66a] prepared isopropyl alcohol by electrolyzing acetone with a 15 per cent solution of sulphuric acid at 6 to 7 volts for 9 hours, using a mercury cathode and lead in 15 per cent sulphuric acid as an anode, the axis of the stirrer being passed through a porous vessel. The cathode liquid is neutralized with concentrated sodium hydroxide and distilled. A 33 per cent yield was obtained.

KETENE

The pyrolytic reactions of acetone are of considerable interest since it has been shown that the highly reactive substance ketene, $CH_2=CO$, is formed by the thermal treatment of acetone at high temperatures and high space velocities, generally in the absence of catalytic materials.

This type of compound was first made by Staudinger,[67] who produced diphenylketene, $(C_6H_5)_2C=CO$, by the action of zinc on diphenylchloroacetyl chloride dissolved in ether and described its properties. The substance reacted readily with oxygen to form an oxidation product (constitution undetermined) insoluble in benzene; with water, to give the corresponding acid; in non-aqueous solutions with hydrogen chloride, to yield the corresponding acid chloride; with alcohols, to form esters; and with ammonia and amines to form the amide and substituted amides, respectively.

Wilsmore[68] found that ketene, $CH_2=CO$, is produced by the action of a hot platinum wire on acetic anhydride, and also when an arc is made to burn beneath the surface of liquid acetic anhydride. He described the chemical properties of this substance, which were similar to those of diphenylketene. Ketene was also obtained by the action of a hot platinum wire on acetone vapors.[69] Other methods of preparation are the passage of acetone vapors through a combustion tube, made of silica, kept at a temperature above 740° C.,[70] and the dehydrogenation of acetaldehyde in the presence of nickel, copper or zinc.[71]

Ketene appears to be stable even at fairly high temperatures, and a 14 per cent yield was obtained by passing the vapors of acetone through a hard glass tube filled with porous earthenware and heated to 500° to 600° C. The decomposition of acetone appeared to take place in two stages: (1) at temperatures of about 500° to 600° C. ketene and methane are the principal products:

$$CH_3COCH_3 \longrightarrow CH_2{=}CO + CH_4$$

and (2) at higher temperatures, ketene is decomposed to yield carbon monoxide and ethylene:

$$2CH_2{=}CO \longrightarrow 2CO + C_2H_4$$

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[65] British Patent 327,224, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 602.

[66] British Patent 316,399, 1928; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1929, 806.

[66a] *Chem.-Pharm. Ind. Russia,* 1932, No. 21; *Chem. Zentr.,* 1932, **2**, 1609; *Brit. Chem. Abs.* **A**, 1933, 143.

[67] *Ber.*, 1905, **38**, 1735.

[68] *J.C.S.*, 1907, 91, 1938; *Chem. Abs.*, 1908, **2**, 798.

[69] Wilsmore and Stewart, *Proc. Chem. Soc.*, 1908, **23**, 309; *Chem. Abs.*, 1908, **2**, 992.

[70] Rice, U. S. Patent 1,879,497, Sept. 27, 1932; assigned to Röhm and Haas Co.; *Chem. Abs.*, 1933, **27**, 313.

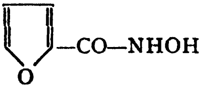
[71] Dreyfus, U. S. Patent 1,870,104, Aug. 2, 1932; *Chem. Abs.*, 1932, **26**, 5315.

Some decomposition of ketene occurs at the lower temperature, particularly with low rates of gas flow.[72]

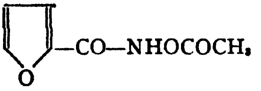
Hurd and Cochran,[73] using a method similar to that mentioned above, were able to increase the yield of ketene to 17.5 per cent by passing the vapors as they issued from the reaction tube through a condenser, thus immediately separating the acetone, as a liquid, from the gaseous ketene. They also showed that ketene is a very active acetylating agent, reacting with hydroxylamine to yield acethydroxamic acid,

$$CH_2{=}CO + NH_2OH \longrightarrow CH_3CONHOH$$

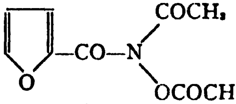
and with pyromucyl-hydroxamic acid to yield the mono- and diacetyl esters.



Pyromucyl-hydroxamic acid



Monoacetyl ester



Diacetyl ester

Ketene can also be prepared by passing the vapors of acetone through a copper tube heated to 650° to 670° C., and packed with copper turnings or those of other metals which melt above 700° C. The period of contact should be less than 5 seconds and the tube must be free from both iron and nickel.[74] An 80 per cent yield of ketene from acetic anhydride or acetone is stated to be obtained with the sulphates of chromium, manganese, aluminum, calcium, barium, strontium, magnesium, or silver or mixtures of these as catalysts[75] at a temperature of 635° C. These sulphates are said to function as "preventive catalysts" and counteract the tendency of the ketene to decompose. Ketenes may also be obtained by passing an aliphatic ketone or a secondary alcohol through a bath of fused metal or inorganic salts.[75a] Ott, Schröter and Packendorff[76] have reported a 50 per cent yield of ketene on passing the vapors of acetone over a heated tungsten filament.

In addition to the reactions previously mentioned ketene reacts with glacial acetic acid to yield acetic anhydride[76a] and with water to form acetic acid.[76b] De Simo,[77] in preparing mixed anhydrides, reacted a ketene with a carboxylic acid of a different number of carbon atoms and subsequently heated the resulting compound to rearrange it into anhydrides of the separate acids.

Ketene is gas at ordinary temperatures; it can be condensed to a liquid boiling at —56° C. and solidifying at —151° C.

HIGHER KETONES

The homologues of acetone are excellent solvents for many purposes, particularly in the cellulose lacquer industry where their higher boiling points make them superior to acetone. The high price and comparative scarcity of these ketones limit their application on a large scale. Provided they can be manufactured at a price not greatly exceeding that of acetone, there is a very wide field for higher ketones.[77a] As previously mentioned, the acetone homologues have heretofore been produced by the distillation of wood or by the dry distillation of the calcium salts of aliphatic acids, the latter being made principally by fermentation processes. The reaction between the vapors of esters and water at elevated temperatures in the presence of catalysts and a small amount of an oxygen-containing gas has been investigated as a method for the preparation of ketones.[78] The possibility of utilizing petroleum hydrocarbons as raw materials for the synthesis of these solvents is also receiving much attention.

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[72] Schmidlin and Bergmann, *Ber.*, 1910, 43, 2821; *Chem. Soc. Abs.*, 1910, 98 (1), 816. See also Peytral, *Bull. soc. chim.*, 1922, 31, 122; *Chem. Abs.*, 1922, 16, 2475.

[73] *J.A.C.S.*, 1923, 45, 515. Modifying this apparatus and using temperatures of 695-705° C., Hurd and Tallyn (*J.A.C.S.*, 1925, 47, 1427) were able to increase the yield of ketene to 35-40 per cent.

[74] Clarke and Waring, U. S. Patent 1,723,724, Aug. 6, 1929; assigned to Eastman Kodak Co.; *Brit. Chem. Abs.* B, 1930, 135.

[75] Nightingale, U. S. Patent 1,602,699, Oct. 12, 1926; assigned to Ketoid Co.; *Chem. Abs.*, 1926. 20, 3697. See also British Patent 237,573, 1924; *J.S.C.I.*, 1925, 863B.

[75a] Standard Oil Development Co., French Patent 742,985, 1933; *Chem. Abs.*, 1933, 27, 3722.

[76] *J. pr. Chem.*, 1931, (3), 130, 177; *Brit Chem. Abs.* A, 1931, 937.

[76a] Ketoid Co., British Patent 237,575, 1924; *Chem. Abs.*, 1926, 20, 1415.

[76b] Berl (British Patent 377,442, 1932; *Chem. Abs.*, 1933, 27, 3949) reacts water (accompanying acetic anhydride formed by cracking acetic acid) with ketene (produced from acetone) to make acetic anhydride.

[77] British Patent 389,049, 1933; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, 27, 4545; French Patent 745,090, 1933; *Chem. Abs.*, 1933, 27, 4250.

Methyl ethyl ketone, $CH_3COCH_2CH_3$. This ketone is a colorless liquid of pleasant odor, boiling at 78.6° C. It is manufactured, together with acetone and other products, by the destructive distillation of wood. Mixtures of ketones are manufactured in France by the distillation of the calcium salts of lower fatty acids and sold under the name of Ketols.[79] The so-called *"Ethyl ketol,"* having a boiling range of 70° to 90° C., consists mainly of methyl ethyl ketone.

The oxidation of secondary butyl alcohol, made by the absorption of butene-1 and butene-2 in sulphuric acid and subsequent hydrolysis, offers a convenient method of preparing this ketone on a commercial scale. Oxidation may be effected in the presence of a silver catalyst. Catalytic dehydrogenation in the presence of copper also yields this ketone. Thus, Sabatier and Senderens [80] obtained methyl ethyl ketone from secondary butyl alcohol by using reduced copper heated to 160° to 300° C., and King [81] dehydrogenated this same alcohol in a similar manner at a temperature of 290° ± 5° C. The secondary butyl alcohol used in the latter work was obtained from butene-2, the yield of the ketone from the crude butene-2 being 70 per cent of the theoretical. The oxidation process, however, possesses advantages over dehydrogenation since the latter sometimes yields undesirable by-products. By the oxidation of secondary butyl alcohol with air in the presence of zinc oxide catalyst, Ottensooser [82] obtained a 93 per cent conversion into the ketone. In the industrial process, the air-alcohol mixture (in the vapor form) is conducted over a catalyst, heated initially to about 500° C. The heat of reaction is then sufficient to maintain the reaction chamber at the necessary temperature. Copper, either alone or alloyed with other metals such as zinc, is the catalyst generally employed.[83]

Another possible method for producing this ketone from petroleum hydrocarbons includes the reduction of methyl vinyl ketone made by the condensation of ethylene with acetyl chloride in the presence of anhydrous aluminum chloride.[84]

Methyl ethyl ketone is an excellent solvent and would replace acetone for many purposes if it could be prepared sufficiently cheaply and in quantity. Its lower vapor pressure renders it less liable than acetone to cause "blushing" in lacquers. This ketone is miscible with castor and linseed oils and with many hydrocarbons and will dissolve cellulose nitrate, ester gum, benzyl abietate, vinyl acetate, and cumarone and other resins. It is partially miscible with water (the ketone dissolves 90 per cent of its weight at 20° C. and water dissolves 24 per cent of its weight of the ketone) with which it forms a constant-boiling mixture (containing 11.4 per cent of water) boiling at 79.6° C. Methyl ethyl ketone is utilized as a solvent, mainly for cellulose esters in lacquers, although it is also used to a very limited extent for the manufacture of certain high grade organic products, such as the perfume, methylionone, and the drug, trional.

[77a] *Cf.* Reid, *Ind. Eng. Chem.,* 1934, **26**, 21.

[78] Roka, Canadian Patent 266,538, 1926; *Chem. Abs.,* 1927, **21**, 917; see also Canadian Patent 262,932, 1926; *Chem. Abs.,* 1926, **20**, 3460; German Patent 544,778, 1925; assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.,* 1932, **26**, 3515.

[79] For the use of the term *Ketol* see Richoux, *Rev. prod. chim.,* 1926, **29**, 150; *Chem. Abs.,* 1926, **20**, 2214.

[80] *Ann. Chim. Phys.,* 1905 (8), **4**, 433, 465; *Chem. Soc. Abs.,* 1905, **88** (1), 401.

[81] *J.C.S.,* 1919, **115**, 1407.

[82] *Bull. soc. chim.,* 1928, **20**, 1380; *Bull. soc. chim.,* 1927, (4) **41**, 324.

[83] Williams and Haller, U. S. Patent 1,450,569, Apr. 3, 1923; Williams and White, U. S. Patent 1,460,876, July 3, 1923; Wells, U. S. Patent 1,497,817, June 17, 1924. Many higher ketones, menthone, cyclohexanone, camphor and acetophenone have been prepared by dehydrogenation of the corresponding alcohol at 120° to 300° C. in the presence of steam, see Sandkuhl, U. S. Patent 1,892,011, Dec. 27, 1932; *Chem. Abs.,* 1933, **27**, 1091; French Patent 696,658, 1930; *Chem. Abs.,* 1931, **25**, 2734; both patents assigned to Rheinische Kampfer-Fabrik G.m.b.H.

[84] Krapiwin, *Bull. Soc. Imp. Nat. Moscow,* 1908, 1; *Chem. Zentr.,* 1910, 1, 1335; I. G. Farbenindustrie A.-G., British Patent 369,313, 1931; *Brit. Chem. Abs.* **B**, 1932, 475.

Di-n-propyl ketone (Butyrone), $CH_3CH_2CH_2COCH_2CH_2CH_3$. This ketone is available in an impure form under the name of amyl ketol, which is manufactured by the dry distillation of calcium butyrate. The calcium butyrate necessary for the process is said to be made by fermentation of saccharified wood in the presence of calcium carbonate. Dipropyl ketone may be produced by interaction of butyraldehyde with steam at 400° to 500° C. in the presence of nickel or cobalt and iron, promoted with an alkaline-earth compound.[85]

In the pure state butyrone boils at 143.5° C. and has d_4^{20} 0.820. It is a solvent for both cellulose nitrate and acetate and also for rubber, natural and synthetic resins of many types, and for linseed and castor oils. It combines these solvent properties with freedom from toxicity under normal working conditions, and a pleasant sweetish odor.

Table 89 summarizes the boiling points and densities of some simple aliphatic ketones.

TABLE 89.—*Aliphatic Ketones.*

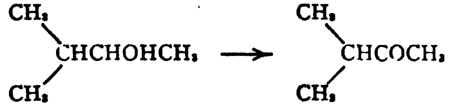
Name	Formula	B.P. ° C. (760 mm.)	d_4^t
Diethyl ketone	$C_2H_5COC_2H_5$	101.1	0.821 (15° C.)
Methyl n-propyl ketone	$CH_3COC_3H_7$	101.8	0.808 (20° C.)
Methyl isopropyl ketone	$CH_3COCH(CH_3)_2$	92.4	0.803 (20° C.)
Methyl n-butyl ketone	$CH_3COC_4H_9$	127.4	0.830 (0° C.)
Methyl n-amyl ketone	$CH_3COC_5H_{11}$	151–152	0.813 (20° C.)

POSSIBLE METHODS OF MANUFACTURE OF THE HIGHER ALIPHATIC KETONES FROM PETROLEUM DERIVATIVES. THE OXIDATION OF SECONDARY ALCOHOLS

All the higher secondary alcohols, amyl, hexyl, and heptyl included, may be converted into ketones by catalytic oxidation with air. These secondary alcohols may be manufactured by methods discussed in Chapter 17 from the low-boiling olefin hydrocarbons of cracked gasoline. Ottensooser,[86] for example, reported that secondary octyl alcohol may be converted into the corresponding ketone (in a yield of 79 per cent of the theoretical) by oxidation with air in the vapor phase at 330° to 340° C. in the presence of a zinc oxide catalyst. In this way it should be possible to find an outlet for the higher secondary alcohols obtained as byproducts of the preparation of secondary butyl alcohol from cracking-gas fractions. By catalytic oxidation, pentanol-2 should yield methyl n-propyl ketone

$$CH_3CH_2CH_2CHOHCH_3 \longrightarrow CH_3CH_2CH_2COCH_3$$

and 3-methylbutanol-2, methyl isopropyl ketone.



$$(CH_3)_2CHCHOHCH_3 \longrightarrow (CH_3)_2CHCOCH_3$$

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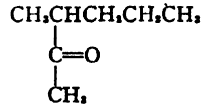
[85] Holzverkohlungs-Industrie A.-G., British Patent 347,593, 1930; *Brit. Chem. Abs.* **B**, 1931, 753.
[86] *Bull. soc. chim.*, 1927, (4) 41, 324; *Chem. Abs.*. 1927, 21, 2089.

APPLICATION OF THE FRIEDEL-CRAFTS REACTION TO PARAFFINIC AND CYCLOPARAFFINIC HYDROCARBONS

A promising development in the realm of hydrocarbon chemistry is the extension of the Friedel-Crafts reaction, which was formerly considered applicable only to aromatic hydrocarbons, to olefins and also to paraffins and cycloparaffins. Not only can organic acid chlorides condense with these hydrocarbons in the presence of condensing agents (e.g., $AlCl_3$), but also with carbon monoxide under pressure, to yield ketones. Descriptions of these condensations have been supplied by Hopff.[87]

The condensation of n-pentane with acetyl chloride was found to take place readily in the presence of aluminum chloride in the cold and the product was proved to be 2-acetylpentane (asymmetrical methyl n-propyl acetone), a liquid (b.p. 136°–140° C.) possessing the constitution

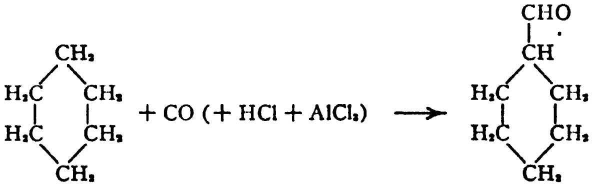


$$CH_3\underset{\substack{|\\ C=O\\ |\\ CH_3}}{C}HCH_2CH_2CH_3$$

From 2500 cc. of n-pentane and 800 grams of acetyl chloride in the presence of 1250 grams of finely powdered anhydrous aluminum chloride Hopff obtained, after decomposition with water, 120 grams of the above ketone together with about 180 grams of a black viscous oil which was not further investigated. The yield of ketone is therefore very poor.

Treatment of 2500 cc. of cyclohexane with 1250 grams of aluminum chloride and 800 grams of acetyl chloride in a similar manner, yielded 800 grams of a yellowish oil volatile with steam, together with 250 grams of a non-volatile dark-colored residue. Fractionation of the former (volatile) liquid yielded 410 grams of a colorless liquid of aromatic odor (b.p. 160°–180° C.) consisting mainly of cyclohexyl methyl ketone. The procedure can be applied also to methane, ethane, and propane but rather less satisfactorily.

Hopff also investigated the reaction of carbon monoxide, under a pressure of 150 atmospheres, with paraffins and cycloparaffins and obtained aldehydes and ketones. Eight hundred grams of cyclohexane and 500 grams of anhydrous aluminum chloride in a 2 liter autoclave with 10 atmospheres of dry hydrogen chloride and 150 atmospheres of carbon monoxide were allowed to stand for 48 hours at ordinary temperature. After decomposition with ice, 135 grams of a liquid volatile with steam was formed. This liquid was extracted with 5 per cent aqueous caustic soda and then distilled, finally yielding about 50 grams of hexahydrobenzaldehyde, b.p. 166°–167° C.



When 100 grams of n-butane were allowed to react with carbon monoxide in the presence of 100 grams of aluminum chloride under a pressure of 130 atmospheres at ordinary temperature (20° C.) for 20 hours, the yield of methyl isopropyl ketone was about 6 grams together with a considerable quantity of other products. In the reaction between carbon monoxide and n-butane a branched-chain ketone is formed:

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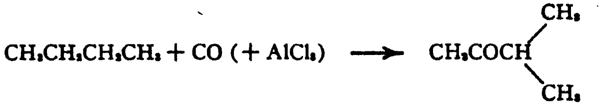
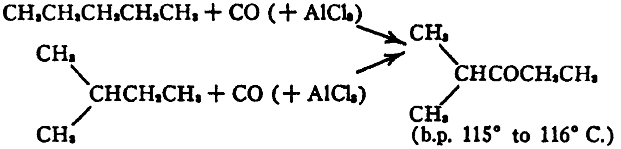
[87] *Ber.*, 1931, **64**, 2739. British Patent 327,411, 1928; *Brit. Chem. Abs.* **B**, 1930, 602; French Patent 671,241, 1928; *Chem. Abs.*, 1930, **24**, 2137; U. S. Patent 1,801,350, Apr. 21, 1931; *Chem. Abs.*, 1931, **25**, 3358, all patents assigned to I. G. Farbenindustrie A.-G.

For similar application of the Friedel-Crafts reaction see Schaarschmidt, French Patent 42,410, 1933; *Chem. Abs.*, 1933, **27**, 4813; French Patent 735,786, 1931; *Chem. Abs.*, 1933, **27**, 991; British Patent 388,734, 1933; *Chem. Abs.*, 1933, **27**, 4538; Mark, Dunkel and Roell, U. S. Patent 1,899,582, Feb. 28, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2961; I. G. Farbenindustrie A.-G., British Patent 391,600, 1933; *Brit. Chem. Abs.* **B**, 1933, 377; Nenitzescu and Cantuniari, *Ber.*, 1932, **65**, 807. See also von Braun, *Ber.*, 1931, **64**, 2869.



$$CH_3CH_2CH_2CH_3 + CO\ (+ AlCl_3) \longrightarrow CH_3COCH(CH_3)_2$$

Ethyl isopropyl ketone was obtained by treating either normal- or iso-pentane with carbon monoxide under pressure in the presence of aluminum chloride. The reactions may be summarized in the following manner:

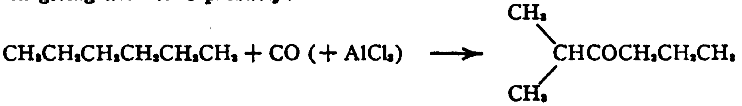


$$CH_3CH_2CH_2CH_2CH_3 + CO\ (+ AlCl_3) \longrightarrow (CH_3)_2CHCOCH_2CH_3$$
$$(CH_3)_2CHCH_2CH_3 + CO\ (+ AlCl_3) \longrightarrow (CH_3)_2CHCOCH_2CH_3$$

(b.p. 115° to 116° C.)

The yield of ethyl isopropyl ketone in either case was, however, poor and relatively large amounts of other products were formed including fatty acids and resins. Thus, by working up the products of the reaction of 108 atmospheres of carbon monoxide on 1 kilogram of n-pentane and 750 grams of aluminum chloride at 50° C. (for five hours), only about 250 grams of crude ethyl isopropyl ketone were secured. Among the acidic products, α-methylvaleric acid was identified. From 1 kilogram of isopentane under similar conditions, only 70 grams of pure ketone were obtained.

Treatment of 1 kilogram of n-hexane with 1 kilogram of aluminum chloride and with carbon monoxide (118 atmospheres pressure) at 50° to 60° C. for 18 hours yielded the following products: 350 grams of unchanged hexane, 520 grams of an oil volatile with steam, and 270 grams of non-volatile oil. The steam-distilled oil was extracted with alkali (acidification of this alkaline extract gave 62 grams of carboxylic acids (b.p. 195° to 240° C.) besides small amounts of higher acids) and distilled to yield 180 grams of liquid boiling up to 160° C. Redistillation gave 18 grams of a liquid (b.p. 135° to 137° C.) which was considered to be n-propyl isopropyl ketone. The reaction giving ketones is probably:



$$CH_3CH_2CH_2CH_2CH_2CH_3 + CO\ (+ AlCl_3) \longrightarrow (CH_3)_2CHCOCH_2CH_2CH_3$$

Although the results of Hopff are of interest, the reported yields of the purified ketones are far too small for the reaction to serve as a technical method for their production. Moreover, large proportions of the original hydrocarbons are converted into aliphatic acids and higher condensation products. In spite of these defects, however, it may be possible to modify the working conditions so as to reduce, in part at least, the formation of by-products.

The direct combination of phosgene with hydrogen and paraffin hydrocarbons to yield either aldehydes or ketones was described by Fohlen.[88] He proposed to effect these combinations in the presence of catalysts consisting of finely divided metals, or their oxides or salts. The following reactions are said to occur between phosgene and hydrogen and methane:

$$COCl_2 + 2H_2 \longrightarrow HCHO + 2HCl$$
$$2CH_4 + COCl_2 \longrightarrow CH_3COCH_3 + 2HCl$$
$$CH_4 + H_2 + COCl_2 \longrightarrow CH_3CHO + 2HCl$$

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[88] French Patent 680,586, 1928; *Chem. Abs.*, 1930, 24, 3799.

KETONES FROM OLEFIN HYDROCARBONS

The condensation of the simple monolefins with organic acid chlorides at low temperatures in the presence of aluminum chloride (or other Friedel-Crafts condensing agents) leads to the production of alkyl vinyl ketones of the general formula

$$R^1R^2C{=}CR^3COC_nH_{2n+1}$$

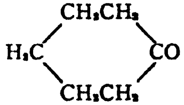
in which R^1, R^2 and R^3 are hydrocarbon radicals or hydrogen. A discussion of this condensation is given in Chapter 24, in which it is pointed out that unstable chloro ketones are formed as intermediates. The yields of vinyl alkyl ketones appear to be good and the process offers a way for the preparation of the higher aliphatic ketones of four and more carbon atoms. The reduction of the alkyl vinyl ketones to saturated ketones involves the hydrogenation of an unsaturated linkage under such conditions that the carbonyl group remains unattacked.

$$R^1R^2C{=}CR^3COC_nH_{2n+1} + H_2 \longrightarrow R^1R^2CHCHR^3COC_nH_{2n+1}$$

The direct alkylation of ketones by olefins was suggested by Brown.[89] The reaction is carried out at temperatures of 250° to 500° C., under pressures of more than 50 atmospheres in the presence of catalysts such as zinc or chromium oxides and zinc chloride. An example of such an operation is the synthesis of propyl methyl ketone from ethylene and acetone. The vapors of acetone and ethylene, in approximately molecular proportions, are slowly led (under 1000 pounds pressure) over a zinc oxide-chromium oxide catalyst maintained at 450° to 500° C. On cooling the exit gases to 0° to 15° C. a liquid mixture of ketones, acetone and ethylene is obtained. The propyl methyl ketone is separated by fractional distillation.

An indirect method of transforming olefins into ketones (or aldehydes) is their conversion into the corresponding oxides followed by isomerization of the latter compounds into substances containing the :CO group. Thus, the isomerization of trimethylethylene oxide to methyl isopropyl ketone in the presence of alumina at 200° to 300° C. was observed by Ipatiev and Leontowitsch.[90] The isomerization of olefin oxides to aldehydes and ketones is effected by heating in the presence of catalysts, such as magnesium pyrophosphate or copper sulphate, with or without the addition of metal oxides, hydroxides, or carbonates, at temperatures of 180° to 300° C.[91]

Of the cyclic ketones, cyclohexanone and the three isomeric methylcyclohexanones are of technical importance. Although they are produced on a large scale from phenol and the cresols, respectively, yet they should be considered as derivatives of naphthene, or petroleum, hydrocarbons.

Cyclohexanone,  $H_2C\begin{matrix}CH_2CH_2\\ \\ CH_2CH_2\end{matrix}CO$, is prepared by the oxidation or catalytic dehydrogenation of cyclohexanol which in turn may be prepared by the hydrogenation of phenol. If the hydrogenation of phenol is carried out at high temperatures the cyclohexanol initially formed undergoes thermal dehydrogenation to cyclohexanone.[92] The oxidation of cyclohexanol with air in the presence of copper gives an excellent yield of this cyclic ketone.

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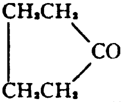
[89] U. S. Patent 1,757,830, May 6, 1930; assigned to Commercial Solvents Corp.; *Chem. Abs.*, 1930, 24, 3247.

[90] *Ber.*, 1903, 36, 2016.

[91] I. G. Farbenindustrie A.-G., British Patent 331,185, 1929; *Brit. Chem. Abs.* B, 1930, 939. British Patent 354,388, 1930; *Brit. Chem. Abs.* B, 1932, 12.

Pure cyclohexanone is a colorless oil (b.p. 156.6° to 156.8° C. and $d^{15.8}_{4}$ 0.9503) and is an excellent solvent for cellulose nitrate and for many natural and synthetic gums and resins. Solutions of cellulose nitrate in this solvent are less viscous than those in ethylene glycol monoethyl ether and exhibit a high tolerance to toluene dilution.[93]

The methylcyclohexanones are prepared by similar methods. A mixture of the three isomeric ketones is marketed as an industrial solvent. The methylcyclohexanones are colorless oils of peppermint-like odor, and possess solvent properties toward cellulose nitrate, yielding solutions which possess rather high viscosities and a high tolerance to toluene dilution.

Another cyclic ketone which may ultimately be produced from cyclopentane of petroleum origin is cyclopentanone,  , a highly reactive ketone (b.p. 129° C. and d^{0}_{20} 0.948). It is obtained in small amounts by the destructive distillation of wood but, on account of its scarcity, as yet has no industrial application. The possibility of making ketones, containing the cyclopentyl ring, from the naphthenic acids of petroleum is discussed in Chapter 48.

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[92] Such reactions are discussed by Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., 1930.

[93] Durrans, "Solvents," Chapman and Hall, London, 1930.

Chapter 19

Sulphur and Sulphur Compounds in Petroleum and Its Distillates. Their Occurrence, Chemical Properties and Possible Applications

The sulphur content of crude petroleum oils from different localities varies over a wide range. For example, the Pennsylvania, Baku, and Rumanian oils contain 0.2 per cent sulphur or less, while those from Ohio, West Texas and California contain from 0.5 per cent to 1.5 per cent or higher. Some California oils have been reported to contain as much as 4 per cent sulphur and many Mexican oils contain as much as 5 per cent.[1] When the crude oil is distilled, under conditions which do not permit cracking of the oil, it is generally found that the sulphur content of the various fractions increases with the boiling range, the residues possessing the highest percentage of sulphur. Curves obtained by plotting the sulphur content against the boiling range of close-cut fractions exhibited a series of rising peaks.[2]

Practically all of the simpler types of organic sulphur compounds have been identified in petroleum oils;[3] these include carbon disulphide, mercaptans, thioethers, thiophenes, thiophanes, organic disulphides and polysulphides, elemental sulphur, and compounds containing both sulphur and oxygen. Hydrogen sulphide is also associated with many high sulphur crude oils. Most of the individual sulphur compounds so far isolated have been found in relatively low-boiling fractions. Of the organic sulphides occurring in oils boiling above 230° C. diphenyl sulphide appears to be the only one which has been identified.

From the refiner's view the two principal objections to the presence of sulphur compounds in distillates, particularly the gasoline and kerosene fractions, are their corrosive properties and their odor. Hydrogen sulphide and mercaptans produce the most objectionable odors, and in both instances this can be easily remedied. Hydrogen sulphide is removed by washing the distillates with dilute solutions of alkalies, either sodium hydroxide or sodium carbonate. The mercaptans, while not so easily removed, can be converted to disulphides (sweetening) which impart a less disagreeable odor to petroleum distillates than the original substances. In addition to their unpleasant odor, mercaptans are strong positive catalysts for gum formation, particularly in gasolines made by cracking.[4]

Corrosion by sulphur compounds may be divided into two types: that caused by these compounds themselves when the petroleum distillates containing them

[1] Gurwitsch and Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, **1932**, 153. Engler-Höfer, "Das Erdöl," Verlag von S. Hirzel, Leipzig, **1913**, 1, 468. For the analysis of California crude oils see Kraemer, *Bur. Mines Rept. of Investigations* **3074**, 1931; *Chem. Abs.*, 1931, **25**, 4390.

[2] Malisoff, private communication.

[3] Challenger, *Chem. and Ind.*, 1929, **48**, 622; *Chem. Abs.*, 1929, **23**, 4332; *Brennstoff-Chem.*, 1929, **10**, *277*; *Chem. Abs.*, 1930, **24**, 493. For bibliography of the sulphur compounds which have been identified in petroleum, shale and tar oils, see Borgstrom and Reid, *Oil and Gas J.*, 1927, **26**, 352. Marcusson, *Mitt. k. Materialprüf.*, 1917, 374; *Z. angew. Chem.*, 1918, **31**, (II), 62; *Chem. Abs.*, 1918, **12**, 2435. Richardson and Wallace, *J.S.C.I.*, 1902, **21**, 316. Shipley, *Can. J. Research*, 1932, **8**, 119; *Chem. Abs.*, 1933, **27**, 2287.

[4] Kruber and Schade, *Brennstoff-Chem.*, 1933, **14**, 124; *Brit. Chem. Abs.* **B**, 1933, 418.

are allowed to remain in contact with metals for some time, and that resulting from the formation of sulphur dioxide (and subsequently sulphuric acid) when the distillates are used in internal-combustion engines.

With respect to the first type of corrosion, Schmidt[5] found that the order of decreasing activity is: mercaptans,[6] elemental sulphur, alkyl sulphates, alkyl sulphides, disulphides, sulphur oxides, carbon disulphide and thiophenes. Heat increases the corrosive action of all of these, and water especially increases the corrosive action of alkyl sulphates by their hydrolysis to yield sulphuric acid. In general, those sulphur compounds which tend to ionize, such as mercaptans, are the most corrosive.

Opinions differ widely as to the amount of sulphur permissible in distillates, such as gasoline for use in internal-combustion engines. For example, Diggs[7] concluded from his experiments that 0.1 per cent sulphur is probably a fair allowable upper limit to avoid excessive corrosion of wrist pins, pistons and rings. This corrosion he explained in the following manner: during combustion of the fuel, sulphur dioxide, water vapor and carbon dioxide are formed. The sulphur dioxide reacts with the condensed water vapor and oxygen of the air to form sulphuric acid, and the sulphuric acid in turn attacks the metallic parts. Mougey[8] on the other hand contended that, with elimination of the condensation of water vapor by crankcase ventilation and thermostatic control of the water jacket temperatures, sulphur corrosion is so greatly reduced as to allow the use of fuels containing as much as 0.25 per cent sulphur. Rackwitz and von Philippovich[9] have also reported that ventilators, thermostats and oil filters permit the use of a fuel containing 0.25 to 0.35 per cent sulphur. Egloff, Lowry and Truesdell[10] reported that the United States is the only country, so far as is known, in which a limit is imposed on the sulphur content of gasoline, and that in Europe, where no limit is set, corrosion due to sulphur is practically unknown.

In this chapter the sulphur derivatives of petroleum are considered with respect to their chemistry, isolation and possible utilization. Refining methods which have as their object primarily the elimination or removal of sulphur compounds from petroleum distillates are mentioned only when they illustrate specifically some of the chemical properties of these sulphur derivatives. More work along the lines indicated has been done with the simpler sulphur derivatives in petroleum, such as elemental sulphur, hydrogen sulphide and mercaptans, than with the more complex compounds, for example, the thioethers and thiophene. For this reason the chemistry of the former is discussed in more detail than that of the latter.

HYDROGEN SULPHIDE

Hydrogen sulphide, which is a gas at ordinary temperatures and pressures, is frequently found in crude petroleum or its distillates, particularly in high sulphur crudes and their derivatives. It is generally more soluble in petroleum hydrocarbons than in water. Table 90 gives the solubility of hydrogen sulphide in water and a number of hydrocarbons at 20° C., the figures representing the number of volumes of the gas dissolved in a unit volume of solvent.[11]

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[5] *Petroleum Z.*, 1927, **23**, 646; *Chem. Abs.*, 1927, **21**, 2785.

[6] Ward, Jordan and Fulweiler (*Ind. Eng. Chem.*, 1932, **24**, 1238) report that mercaptans catalyze gum formation. For a discussion of gum formation see Chapter 40.

[7] *Ind. Eng. Chem.*, 1928, **20**, 16.

[8] *Ind. Eng. Chem.*, 1928, **20**, 18.

[9] *Luftfahrtforschung*, 1929, **5**, No. 4, 157; *Chem. Abs.*, 1930, **24**, 3891.

[10] *Nat. Pet. News*, 1930, **22** (24), 41; **22** (25), 69; **22** (26), 79; *Chem. Abs.*, 1930, **24**, 5473.

[11] Values for organic liquids as given by Bell (*J.C.S.*, 1931, 1376); value for water, by Schönfeld (*Ann.*, 1855, **93**, 26).

TABLE 90.—*Solubility of Hydrogen Sulphide in Water and Some Organic Solvents.*

Solvent	Volumes of H_2S Dissolved per Unit of Solvent at 20° C.
Water	2.905
Hexane	6.30
Octane	6.80
Dodecane	5.71
Cyclohexane	7.50
Benzene	15.68
Toluene	16.90

The presence of hydrogen sulphide in the various distillates is undesirable because of danger to workingmen (it is toxic), corrosion of equipment, fires caused by the rapid oxidation of the iron sulphide formed by hydrogen sulphide corrosion, and lastly the oxidation of hydrogen sulphide itself (by the oxygen of the air) to water and elemental sulphur.

The uses of hydrogen sulphide, outside of the laboratory, are rather limited. Its salts, however, such as sodium sulphide, have been used as aids in the dyeing of cotton fiber with sulphur dyes, as reducing agents or otherwise in the preparation of dyestuffs, as depilatories for hides and skins, and as denitrating agents for artificial silk.

One method of extracting hydrogen sulphide from petroleum is by washing the various fractions with dilute alkaline solutions. It may be done also by adding the alkaline solution to the distillate stream as the latter comes from the fractionating column on the still to the run-down tank.[12] Such processes are based on the fact that hydrogen sulphide possesses acidic properties and reacts with bases to form compounds according to the following reactions:

$$NaOH + H_2S \longrightarrow NaHS + H_2O$$
$$NaHS + NaOH \longrightarrow Na_2S + H_2O$$

As pointed out later the alkaline solutions used in the extraction of hydrogen sulphide from some distillates also dissolve a part of the low-boiling mercaptans. These mercaptans can be recovered by the distillation of the alkaline solutions.

For refining petroleum distillates several modifications of this method have been suggested. For example, solutions of a mixture of sodium bicarbonate and carbonate[13] and of sodium tetrathionate[14] have been recommended for the removal of hydrogen sulphide. In the first instance the reagent, after use, may be regenerated by aeration in the presence of a small quantity of either nickel or cobalt sulphide to serve as a catalyst. It has been reported that when large quantities of hydrogen sulphide are to be removed the addition of zinc sulphate to caustic soda solution gives better results.[15]

Another reagent proposed for the removal of hydrogen sulphide is brucite, or magnesium hydroxide.[16] The gasoline, or other petroleum distillate, is agitated with a suspension of this base in water, and hydrogen sulphide is removed as magnesium hydrosulphide, according to the equation:

$$Mg(OH)_2 + 2H_2S \rightleftharpoons Mg(SH)_2 + H_2O$$

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[12] Faught, *Refiner*, 1931, 10 (4), 179; *ibid.*, 1931, 10 (5), 70; *Chem. Abs.*, 1931, 25, 4112.
[13] Rosenstein, U. S. Patent 1,827,912, Oct. 20, 1931; *Chem. Abs.*, 1932, 26, 837.
[14] Rosenstein, U. S. Patent 1,832,325, Nov. 17, 1931; *Chem. Abs.*, 1932, 26, 839.
[15] *Refiner*, Dec. 1931, 87.
[16] Gardner and Higgins, *Ind. Eng. Chem.*, 1932, 24, 1140; Higgins, *Nat. Pet. News*, 1933, 25 (15), 26; *Chem. Abs.*, 1933, 27, 3594; *Oil and Gas J.*, 1933, 31 (50), 10.

At ordinary temperatures this reaction proceeds mainly toward the right, while at elevated temperatures it is reversed, affording an easy method of regenerating the spent brucite. As neither the hydroxide nor the hydrosulphide of magnesium is very soluble in water, it is often necessary to extract several times to free a distillate of a high percentage of hydrogen sulphide. This reagent has been used successfully in the extraction of hydrogen sulphide not only from distillates, but also from still gases, natural gas, and crude oils.

Several methods are available for the removal of hydrogen sulphide from still gases. One method is to wash the gas with a solution of sodium or potassium carbonate.[17] The spent carbonate solution can be regenerated afterwards by passing carbon dioxide through it, to expel the hydrogen sulphide, followed by heating, to convert the bicarbonates to carbonates. In the Koppers [18] process the alkaline solution, sodium carbonate or phosphate, is regenerated by adding a sulphide, such as nickel sulphide, and oxidizing the solution with air. Free sulphur rises to the surface of the solution and may be skimmed off. Sodium carbonate solutions, used for the absorption of hydrogen sulphide, may be regenerated by heating and aeration,[19] or by passage over iron compounds,[20] such as the oxide, carbonates, or basic carbonate. Suspensions of the hydroxides, oxides, carbonates or basic carbonates of magnesium, barium, calcium or strontium in an alkaline solution may be employed as the absorbing media.[21] Other solvents suggested for washing the gases to absorb hydrogen sulphide are solutions of a compound of ammonium thiosulphate and sulphur dioxide,[22] a mixture of sulphites and bisulphites,[22a] ammonium tetrathionate and thiosulphate,[22b] potassium hydroxide and boric acid,[22c] and alkaline solution of potassium ferricyanide,[23] lime water,[23a] aqueous ammonia,[23b] aqueous sulphur dioxide,[23c] or potassium phosphate.[23d] Absorption of hydrogen sulphide with water alone has been employed.[23e] Mann and Lebo [23f] used a suspension of iron oxide in caustic soda solution and regenerated the mixture, which had been converted to iron sulphide suspended in an alkaline solution, by blowing with air. Free sulphur is formed and removed in the foam produced during oxidation. Klempt and Brodkorb[23g] recommended ferric hydroxide sludge in aqueous ammonia for this purpose.

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[17] Petit, U. S. Patent 1,598,985, Sept. 7, 1926; *Chem. Abs.*, 1926, **20**, 3558. British Patent 195,061, 1923; *J.S.C.I.*, 1923, **42**, 929A. Wagner (U. S. Patent 1,918,153, July 11, 1933; assigned to Pure Oil Co.; *Chem. Abs.*, 1933, **27**, 4664) proposed scrubbing the gas under pressure with a saturated solution of sodium bicarbonate. The absorbed hydrogen sulphide is later liberated by passing the bicarbonate solution in contact with flue gases.

[18] British Patent 241,221, 1924; *Chem. Abs.*, 1926, **20**, 2578. British Patent 241,452, 1924; *Chem. Abs.*, 1926, **20**, 3558.

[19] Koppers Co., British Patents 190,115, 190,116 and 190,117, 1922; *Chem. Abs.*, 1923, **17**, 2952.

[20] Koppers Co., British Patents 190,119 and 190,131, 1922; *Chem. Abs.*, 1923, **17**, 2952.

[21] Koppers Co., British Patent 190,118, 1922; *Chem. Abs.*, 1923, **17**, 2940; British Patent 255,144, 1925; *Chem. Abs.*, 1927, **21**, 2784.

[22] Hansen, U. S. Patent 1,854,511, Apr. 19, 1932; assigned to Koppers Co.; *Brit. Chem. Abs.* **B**, 1933, 214.

[22a] Hansen, *Chem.-Ztg.*, 1933, **57**, 25; *Brit. Chem. Abs.* **B**, 1933, 226. I. G. Farbenindustrie A.-G., British Patent 367,343, 1930; *Chem. Abs.*, 1933, **27**, 2564. Bähr, German Patent 570,243, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2564.

[22b] Overdick, German Patent 576,162, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3807. Bähr, German Patent 575,134, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3590. Hansen, Werres, Hiller and Voituret, *Chem.-Ztg.*, 1933, **57**, 361, 382; *Chem. Abs.*, 1933, **27**, 3803.

[22c] Bragg, U. S. Patent 1,920,626, Aug. 1, 1933; assigned to Koppers Co.; *Chem. Abs.*, 1933, **27**, 4909.

[23] Fischer, U. S. Patent 1,891,974, Dec. 27, 1932; *Chem. Abs.*, 1933, **27**, 2020.

[23a] Vuiborova and Kalininskaya, *Groznenskii Neftyanik*, 1932, **2**, 56; *Chem. Abs.*, 1933, **27**, 4057. Corner and McGinn, British Patent 376,383, 1931; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, **27**, 2565. *Cf.* Bálint, Hungarian Patent 105,323, 1933; *Chem. Abs.*, 1933, **27**, 4061.

[23b] Korobchanskii, *Coke and Chem.* (*U.S.S.R.*), 1932, No. 8, 68; *Chem. Abs.*, 1933, **27**, 3585.

[23c] Melvill, British Patent 370,911, 1931; *Chem. Abs.*, 1933, **27**, 2564.

[23d] Rosenstein, *Petroleum*, 1933, **29** (24), 4; *Brit. Chem. Abs.* **B**, 1933, 690.

[23e] Jacobson, U. S. Patent 1,900,398, Mar. 7, 1933; assigned to Koppers Co.; *Chem. Abs.*, 1933, **27**, 3063.

[23f] U. S. Patent 1,525,140, Feb. 3, 1925; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1925, **19**, 1035. See also Sperr, U. S. Patent 1,854,770, Apr. 19, 1932; assigned to Koppers Co.; *Brit. Chem. Abs.* **B**, 1933, 214.

Aqueous solutions of triethanolamine, or of a mixture of ethanolamines, are employed for the removal of hydrogen sulphide from gases.[24]

Activated charcoal[24a] was recommended for the adsorption and catalytic oxidation of hydrogen sulphide. Ferric oxide and hydroxide,[24b] silica gel,[24c] or bauxite,[24d] and a metallic oxide (e.g., iron oxide) have been suggested for the same purpose. The capacity of ferric oxide for removing hydrogen sulphide is increased by the addition of activated carbon.[24e] Nickel oxide, together with an oxygen-transferring element of Groups IV to VI of the periodic table and 10 per cent of lead or bismuth, has been employed.[24f] Another method is the preferential oxidation of hydrogen sulphide and organic sulphides, by a mixture of metallic oxides such as those of copper and chromium, or copper, chromium and uranium.[24g]

SOME APPLICATIONS OF HYDROGEN SULPHIDE

The complete removal of hydrogen sulphide from gaseous mixtures, which are to undergo further treatment, is oftentimes undesirable. For example, in the treatment of hydrocarbon gases with steam at 1000° C. in the presence of a chromium catalyst to yield hydrogen and carbon monoxide, the efficiency of the catalyst is said to be increased if about one per cent of hydrogen sulphide, or other gaseous sulphur compounds, are present in the reaction mixture.[25]

Under certain conditions hydrogen sulphide will react with gaseous hydrocarbons, particularly at high temperatures. For example, Wheeler and Francis[26] have reported that when a gas containing methane, ethane and propane is mixed with 12.5 per cent hydrogen sulphide and the mixture is passed at the rate of 250 reciprocal minutes through a reaction chamber heated to 1200° C., both carbon disulphide and benzene are obtained. The yields of these substances are about 0.6 gallon of carbon disulphide and 0.3 gallon of benzene per 1000 cubic feet of gas. Olefinic gases and gases normally containing hydrogen sulphide or other sulphides, such as natural gas, are said to react in a similar manner.

Ethylenic hydrocarbons, such as ethylene, propylene, butylene or isoamylene, react with hydrogen sulphide at 650° to 725° C. in the presence of silica gel.[27] A variety of products are obtained, including hydrogen, methane, ethylenic and saturated hydrocarbons, aromatics, mercaptans, thioethers, thiophene and its homologues and carbon bisulphide. With respect to the formation of sulphur compounds, the mercaptans are formed by the interaction of the unsaturated hydrocarbons and hydrogen sulphide. Decomposition of the mercaptans yields thioethers, and the latter in turn give thiophene and its homologues. Butyl sulphide or mercaptan in the presence of silica gel at 700° C. was converted into thiophene.[28] The proportion of carbon bisulphide was greater at the higher temperatures.

[23g] German Patent 568,638, 1929; assigned to Gesellschaft für Kohlentechnik m.b.H.; *Chem. Abs.*, 1933, **27**, 2790.

[24] This procedure is discussed in Chapter 23.

[24a] Koenigstuhl, *Coke and Chem.* (*U.S.S.R.*), 1932, No. 7, 32; *Chem. Abs.*, 1933, **27**, 3585. I. G. Farbenindustrie A.-G., British Patent 370,466, 1930; *Chem. Abs.*, 1933, **27**, 2564. Goetze, U. S. Patent 1,911,498, May 30, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4061.

[24b] Docking, British Patent 368,426, 1930; assigned to Premix Gas Plants Ltd.; *Chem. Abs.*, 1933, **27**, 2563.

[24c] Miller and Connally, U. S. Patent 1,895,724, Jan. 31, 1933; assigned to Silica Gel Corp.; *Chem. Abs.*, 1933, **27**, 2567.

[24d] Thompson, U. S. Patent 1,922,872, Aug. 15, 1933; assigned to General Chemical Co.; *Chem. Abs.*, 1933, **27**, 5175.

[24e] Olin, Scarth and Starkweather, *Gas Age-Record*, 1932, **70**, 561; *Chem. Abs.*, 1933, **27**, 2281.

[24f] Baehr, U. S. Patent 1,900,751, Mar. 7, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 3063.

[24g] Huff, Logan and Lusby, British Patent 305,026, 1929; *Brit. Chem. Abs.* **B**, 1930, 1012. Lusby, U. S. Patent 1,900,882, Mar. 7, 1933; assigned to Huff; *Chem. Abs.*, 1933, **27**, 3063. Henglein and Hagenest, German Patent 558,940, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 543.

[25] Goodfellow and Spencer, British Patent 370,457, 1931; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 600.

[26] British Patent 351,994, 1930; U. S. Patent 1,907,274, May 2, 1933; *Chem. Abs.*, 1933, **27**, 3487; both patents assigned to Imperial Chemical Industries, Ltd.

[27] Mailke and Renaudie, *Compt. rend.*, 1932, **195**, 391; *Brit. Chem. Abs.* **A**, 1932, 928. Other examples of the preparation of mercaptans from hydrogen sulphide and olefins are given in Chapter 25.

Acetylene and hydrogen sulphide react at a temperature of 320° C. in the presence of bauxite to yield a product, containing about 30 per cent sulphur, from which almost pure thiophene may be obtained by fractional distillation. In the presence of a catalyst consisting of nickel hydroxide and cement at a temperature of 300° C. these same reactants yield a product high in sulphur from which mercaptans, thiophene and methyl thiophene may be separated by fractionation.[29]

ELEMENTAL SULPHUR

The presence of elemental sulphur in various petroleum distillates probably results from the decomposition of complex sulphur compounds during distillation as well as the oxidation of hydrogen sulphide. It no doubt also occurs naturally in high sulphur crude petroleums and comes over, to some extent at least, during the distillation of the various fractions. As elemental sulphur exerts a high corrosive action on various metals [30] its removal from petroleum distillates is highly desirable.

Petroleum and its distillates cannot be regarded in any sense as a source of raw elemental sulphur for two reasons: first, because of the very small percentage of it actually present, and, second, because of the difficulties of extracting it as such. Furthermore, abundant natural sources of sulphur are available from which this element is obtained much more economically than by any procedures so far suggested to recover it from petroleum. The discussion of sulphur extraction from petroleum oils is therefore limited to its removal from these oils on account of its corrosive properties.

Several methods for the removal of elemental sulphur are based on its reactions with alkali or alkaline earth sulphides to form the corresponding polysulphides. Sodium sulphide (Na_2S), for example, yields a series of polysulphides varying in composition from Na_2S_2 to Na_2S_5. Another reaction often employed is that between elemental sulphur and soluble lead mercaptides, whereby lead sulphide and organic disulphides are formed. This reaction is known as *sweetening* and is discussed in more detail later.

Cobb [31] has suggested heating the oil with caustic alkali, such as sodium hydroxide, or calcium hydroxide, and hydrogen sulphide. Treating oil containing both hydrogen sulphide and sulphur with an alkaline solution and heating [32] has also been proposed. In both instances the alkali sulphide first formed reacts with elemental sulphur to form the alkali polysulphide. Calcium sulphide may be used [33] in place of the alkali. Youtz and Perkins [34] used a concentrated solution of sodium sulphide for the same purpose.

The use of "spent doctor" (sodium plumbite solution which has been used in the treatment of "sour" distillates) has been proposed by Simpson.[35] The effectiveness of this reagent is probably due to the sodium sulphide, or mercaptides, produced in the treatment of the distillate. Sodium sulphide reacts with sulphur to form water-soluble polysulphides, and sodium mercaptides with the sulphur yield sodium sulphide and organic disulphides.

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[28] Malisoff and Marks (*Ind. Eng. Chem.*, 1931, 23, 1114) report that mercaptans are thermally decomposed at temperatures of about 475° C. to yield hydrogen sulphide and the corresponding olefin.

[29] Stuer and Grob, U. S. Patent 1,421,743, July 4, 1922; *Chem. Abs.*, 1922, 16, 3093.

[30] Schmidt, *loc. cit.*

[31] U. S. Patent 1,357,224, Nov. 2, 1920; *Chem. Abs.*, 1921, 15, 311.

[32] Cobb, U. S. Patent 1,413,005, April 18, 1922; *Chem. Abs.*, 1922, 16, 2220. See also Stratford, McIntyre and Moor, U. S. Patent 1,838,031, Dec. 22, 1932; *Chem. Abs.*, 1932, 26, 1432; Stratford and Doohan, U. S. Patent 1,904,173, Apr. 18, 1933; *Chem. Abs.*, 1933, 27, 3325; both patents assigned to Standard Oil Development Co.

[33] Cobb, U. S. Patent 1.357,225, Nov. 2, 1920; *Chem. Abs.*, 1921, 15, 311.

[34] *Ind. Eng. Chem.*, 1927, 19, 1247.

Wendt and Diggs[36] have pointed out that some sour distillates contain sufficient elemental sulphur, in addition to mercaptans, to precipitate lead sulphide immediately on agitating with sodium plumbite solution and to sweeten the distillate without the addition of sulphur. This, of course, removes the elemental sulphur. Such a process may also be applied by mixing a distillate containing mercaptans with one containing elemental sulphur and then agitating the mixture with sodium plumbite solution.

Vesselovsky and Kalichevsky[37] suggested the use of potassium or sodium hydroxide dissolved in organic solvents such as absolute ethyl or isopropyl alcohols, absolute ether, or 91 to 98 per cent isopropyl alcohol. Of the two alkalies, potassium hydroxide reacts the more rapidly to produce potassium thiosulphate, polysulphides and water. The following reaction has been suggested by these investigators as taking place initially:

$$6KOH + 6S \longrightarrow K_2S_2O_3 + 2K_2S_2 + 3H_2O$$

This is very probably followed by reaction of potassium disulphide with elemental sulphur to yield the trisulphide and possibly higher sulphides.

The use of an alkali sulphide dissolved in a non-aqueous solvent (for example, mono- or di-hydric alcohols, ketones or epichlorohydrin) was suggested by Malisoff.[38] The alkali sulphide (or polysulphide) in an organic solvent (methanol) is stated to have a reducing action on organic disulphides.

It appears possible not only to remove elemental sulphur but other types of sulphur compounds as well in a single operation. For example, Dormon[39] proposed treating gasoline, or higher distillates, with nickel or other metals in rotating cells, and Bruzac[40] suggested distilling the heavier oils (at temperatures not exceeding 500° C.) in the presence of metals (iron, copper or nickel). Washing dry, finely ground potassium hydroxide with gasoline is reported by Wilson[41] to reduce materially its sulphur content. Faught[42] described a process in which gasoline vapors are treated with sodium vapors, which not only remove sulphur with the formation of sodium sulphide but gum-forming compounds as well. Treatment of the distillates with lead, mercury, or copper, or their amalgams or oxides at temperatures below 80° C. was recommended by Mossgraber.[43]

[35] U. S. Patent 1,718,713, June 25, 1929; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1929, **23**, 4061. See also Wagner, *Oil and Gas J.*, 1933, **31** (45), 58; *Chem. Abs.*, 1933, **27**, 3594.

[36] *Ind. Eng. Chem.*, 1924, **16**, 1113.

[37] *Ind. Eng. Chem.*, 1931, **23**, 181.

[38] U. S. Patent 1,899,042, Feb. 28, 1933; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 2799.

[39] U. S. Patent 1,828,734, Oct. 27, 1931; assigned to Basic Patents Corp.; *Chem. Abs.*, 1932, **26**, 839.

[40] British Patent 346,153, 1929; assigned to M. Mercurio; *Chem. Abs.*, 1932, **26**, 589.

[41] U. S. Patent 1,805,444, May 12, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1932, 92.

[42] *Refiner*, 1932, **11** (4), 273. Other processes employing metallic sodium as a refining agent are described by: Deichler and Lesser, German Patent 160,717, 1904; *Chem. Zentr.*, 1905, **2**, 731. Knibbs, British Patent 154,464, 1919; *J.S.C.I.*, 1921, **40**, 38A. Erdöl- und Kohle-Verwertung A.-G., German Patent 469,228, 1921; *Chem. Abs.*, 1929, **22**, 2291. Watson, U. S. Patent 1,474,395, Nov. 20, 1923; *Chem. Abs.*, 1924, **18**, 584. Carlisle, Canadian Patent 300,843, 1930; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1930, **24**, 3639. See also Conant and Blatt, *J.A.C.S.*, 1928, **50**, 542. Procedures involving the use of alkali or alkaline-earth metals are described by: Fields, U. S. Patent 1,864,719, June 28, 1932; *Brit. Chem. Abs.* **B**, 1933, 535. Magill, U. S. Patent 1,890,881, Dec. 13, 1932; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1933, **27**, 1743. Cross, U. S. Patent 1,865,235, June 28, 1932; assigned to Cross Development Co.; *Brit. Chem. Abs.* **B**, 1933, 537. *Cf.* Hofmeier and Wisselinck, *Brennstoff-Chem.*, 1933, **14**, 286; *Brit. Chem. Abs.* **B**, 1933, 819.

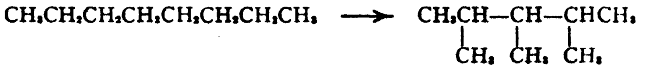
[43] British Patent 368,882, 1930; *Chem. Abs.*, 1933, **27**, 2293.

REACTION OF SULPHUR WITH PARAFFIN HYDROCARBONS

As previously pointed out, elemental sulphur may exist as such in crude petroleum or may be formed by the decomposition of complex organic sulphur compounds during the distillation processes. At such temperatures, or at higher temperatures as in cracking operations, elemental sulphur itself reacts with petroleum hydrocarbons to yield various sulphur compounds. A review of the possible reactions which may take place should therefore be of interest.

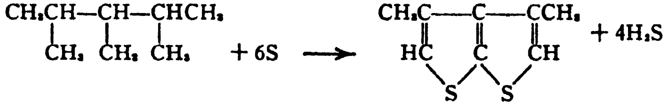
The paraffin hydrocarbons of lower molecular weights generally react very slowly, if at all, with sulphur. Spanier[44] has shown that n-hexane and sulphur do not react appreciably when heated for 24 hours at 210° C. At 300° to 350° C. and over long periods of heating, n-butane and n-heptane yielded, with sulphur, some thiophene and thiophene derivatives, respectively. At higher temperatures, however, reaction does take place as Fletcher, Wheeler and McAulay[45] have found that methane at 1100° C. reacts with sulphur vapors to form carbon disulphide. They also stated that at such high temperatures hydrogen sulphide behaves in the same way as sulphur vapors.

On heating n-octane with sulphur in sealed tubes at 270° to 280° C. Friedmann[46] obtained small quantities of a thiophene, $C_8H_{12}S$, and of a thiophthen, $C_8H_8S_2$. The formation of such cyclic compounds from a straight-chain hydrocarbon was thought to take place in two steps: first, the rearrangement of n-octane into a branched-chain hydrocarbon:



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow CH_3\underset{CH_3}{CH}-\underset{CH_3}{CH}-\underset{CH_3}{CH}CH_3$$

and, second, the reaction of the branched-chain hydrocarbon with sulphur to yield the cyclic compound:



The thiophene derivative, $C_8H_{12}S$, in many respects resembled the diethylthiophene described by Muhlert;[47] and the reactions of the thiophthene derivative, $C_8H_8S_2$, indicated it to be the dimethylthiophthene.

On heating higher molecular weight paraffins with sulphur, hydrogen sulphide and carbon disulphide are the principal gaseous products. No identification of any intermediate products appears yet to have been made. Thus, Siebeneck[48] found on heating paraffin wax with sulphur that hydrogen sulphide evolution began at 150° C., and at 230° C. both this substance and carbon disulphide were being evolved. After 7 hours heating the final product obtained was a substance corresponding to the formula $(C_5S)_x$, which was insoluble in organic solvents.

The reaction of paraffins with sulphur to yield hydrogen sulphide has been suggested as a means of preparing this compound. For example, Prothière[49] obtained 48.2 liters of hydrogen sulphide from 70 grams of sulphur and 30 grams of petrolatum. Gfeller and Schaeffer[50] recommended using a mixture of 25 grams of paraffins, 15 grams of sulphur and 5 grams of asbestos fiber. For preparing small quantities of hydrogen sulphide 0.5 to 2.0 cc. of the mixture are heated in a test tube. The evolution of the gas ceases when the source of heat is withdrawn. These investigators represented the reaction by the equation:

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[44] Kahlsruhe Dissertation, 1910; see also Gurwitsch and Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, 1932, 95.

[45] British Patent 331,734, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1930, 862.

[46] *Ber.*, 1916, 49, 1344; *Chem. Soc. Abs.*, 1916, 110 (1), 735.

[47] *Ber.*, 1886, 19, 633.

[48] *Petroleum Z.*, 1922, 18, 281; *Chem. Abs.*, 1922, 16, 3200.

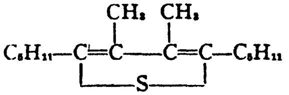
[49] *Pharm. Zeit.*, 48, 78; *Chem. Zentr.*, 1903, 1, 492.

$$C_nH_{2n+2} + S_{n+1} \longrightarrow (n+1)\,H_2S + C_n$$

Bindschedler and Rugeley[51] produced hydrogen sulphide by heating a mixture of hydrocarbon oil and sulphur and purified the gas by passing it through charcoal or some other absorption agent. Scudder and Lyons[51a] investigated the effect of cadmium sulphide, iron, aluminum, zinc, copper, cobalt, lampblack, charcoal, anhydrous aluminum chloride and many other substances on the temperature of initial reaction of sulphur and paraffin. Lampblack and anhydrous aluminum chloride proved to be the best catalysts.

REACTION OF SULPHUR WITH UNSATURATED HYDROCARBONS

In studying the reactions between olefins and sulphur heated under pressure, Friedmann[52] obtained from hexylene and sulphur the following compounds: $C_6H_{12}S$, boiling point 40-41° C. at 10 mm.; $C_{12}H_{14}S$, boiling point 112-113° C. at 10 mm.; and $C_{18}H_{30}S$, boiling point 128° C. at 10 mm. The residue left after the distillation of the reaction products was an asphaltic material whose composition corresponded to the formula $C_{24}H_{20}S_2$. No definite compounds were obtained when n-octylene was heated with sulphur. With methyl-n-amylethylene and sulphur, the thiophene and thiophthene derivatives, $C_8H_{12}S$ and $C_8H_8S_2$ respectively, obtained were the same as those from n-octane, and in addition the two compounds $C_{16}H_{28}S$, and $C_{24}H_{38}S_2$ were formed. The chemical properties of the former indicated that it possessed the structural formula corresponding to



The other compound may have been formed by the condensation of 1 molecule each of $C_8H_{12}S$ and $C_{16}H_{28}S$.

Unsaturated hydrocarbons, containing eight or more carbon atoms, produced by the action of ammonia or other alkalies on di- and poly-chlorinated hydrocarbons, yield various sulphur derivatives when treated with sulphur (or sulphur compounds) by heating under pressure. Oxidation of such derivatives by nitric acid, hydrogen peroxide, or potassium permanganate leads to the formation of sulphonic acids, which have possible uses in the textile industry and in medicine.[53]

REACTION OF SULPHUR WITH CYCLIC HYDROCARBONS

When naphthenes are heated with sulphur, dehydrogenation takes place, accompanied by the evolution of hydrogen sulphide. Markownikow and Spady[54] reported that on boiling octanaphthene, obtained from Caucasian petroleum, with sulphur a small quantity of metaxylene was formed. This was identified by converting it to the trinitro compound, and to mono- and di-sulphonic acids. Markownikow and Spady therefore considered the octanaphthene occurring in this fraction to be hexahydroxylene.

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[50] *Schweiz. Apoth. Ztg.*, 1929, **67**, 109; *Chem. Abs.*, 1930, **24**, 4997. See also Nellensteyn and Thoenes, *Chem. Weekblad*, 1932, **29**, 582; *Brit. Chem. Abs.* **A**, 1933, 47.

[51] U. S. Patent 1,565,894, Dec. 15, 1925; assigned to Tubize Artificial Silk Co. of America, *Chem. Abs.*, 1926, **20**, 483.

[51a] *Proc. Indiana Acad. Sci.*, 1931, **40**, 185; *Chem. Abs.*, 1932, **26**, 1234.

[52] *Ber.*, 1916, **49**, 1551; *Chem. Abs.*, 1917, **11**, 1958; *Petroleum*, 1916, **11**, 693; *Chem. Abs.*, 1917, **11**, 3424.

[53] I. G. Farbenindustrie A.-G., British Patents 360,993, 361,356 and 361,357, 1930; *Brit. Chem. Abs.* **B**, 1932, 93.

[54] *Ber.*, 1887, **20**, 1850.

Friedmann,[55] however, suggested that the reaction between sulphur and naphthenes takes place in steps, and that complete dehydrogenation of the hydroaromatic compound to the aromatic does not occur. In fact, dehydrogenation ceases, he believed, with the formation of the dihydride. For example, after heating cyclohexane and sulphur under pressure and fractionating the reaction products under reduced pressure, the lowest boiling fraction on nitration yielded m-dinitrobenzene; from the intermediate fraction boiling between 40° and 60° C. thiophenol was isolated; and in the residue phenyl sulphide was detected. Since benzene was not found among the reaction products Friedmann concluded that dihydrobenzene was present in the lowest boiling fraction, as it would be both oxidized and nitrated by nitric acid to yield m-dinitrobenzene.

The successive steps in the degradation of cyclohexane, according to Friedmann, may be represented by the following equations:

$$C_6H_{12} + S \longrightarrow C_6H_{11}SH$$

$$C_6H_{11}SH \longrightarrow H_2S + C_6H_{10}\ (\textit{cyclohexene})$$

$$C_6H_{10} + S \longrightarrow C_6H_9SH$$

$$C_6H_9SH \longrightarrow H_2S + C_6H_8\ (\textit{cyclohexadiene})$$

The thiophenol may be formed by the reaction of cyclohexadiene with hydrogen sulphide and sulphur:

$$C_6H_8 + 2S + 2H_2S \longrightarrow C_6H_{12}S_4$$

$$C_6H_{12}S_4 \longrightarrow 3H_2S + C_6H_5SH$$

Friedmann also observed that on heating methylcyclohexane with sulphur and fractionating the reaction products, the portion boiling between 100.5° and 120° C. yielded trinitrotoluene on nitration. Thiocresol was isolated from the fraction boiling between 80° and 130° at 11 mm.

The different fractions obtained from the reaction product of 1,3-dimethylcyclohexane and sulphur reacted more or less strongly with bromine or permanganate, indicating the presence of unsaturated compounds. The fraction boiling between 30° and 90° C. at 11 mm. yielded trinitro-m-xylene on nitration, and thio-m-xylene was found in the fraction boiling between 90° and 110° C. at 11 mm., and m,m′-dimethyldibenzyl, in the fraction boiling between 110° and 180° C. at 11 mm. This latter hydrocarbon could be obtained by heating m-xylene and sulphur under pressure.

PRODUCTION OF SULPHUR DYES

Sulphur dyes were made by Palmer and Lloyd[56] by passing either gaseous hydrocarbons or the vapors of higher-boiling hydrocarbons through molten sulphur at 350° to 400° C. For example, acetylene, ethylene, and kerosene yield dyes which are bluish-black solids, and which contain about 68, 61, and 62 per cent, respectively, of sulphur. These dyes are true sulphur dyes as they are soluble in sodium sulphide solution and can be applied directly to cotton, rayon, and other fibers. The dyes are fast to repeated washing with soap and water, and to organic solvents. When applied to cotton or rayon the dye obtained from ethylene imparts a reddish-brown color to the fiber, that from acetylene, a gray color, and that from kerosene, a khaki color.

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[55] *Petroleum*, 1916, 11, 978; *Chem. Soc. Abs.*, 1917, 112 (1), 14.
[56] *J.A.C.S.*, 1930, 52, 3388.

Numerous other organic substances react with sulphur in a similar manner, for example, aromatic hydrocarbons (such as benzene, toluene and diphenyl), amines (such as aniline or diethylaniline), aldehydes, ethers, acids and alcohols. All of the dyes so produced possess a high sulphur content, usually about 60 to 80 per cent, except that from ethyl alcohol which contains only about 10 per cent sulphur.

MERCAPTANS

In the petroleum industry more work has probably been done with mercaptans and a better knowledge of their chemistry obtained than with any other class of sulphur compounds. The reasons for this are apparent since, as a class, the mercaptans react readily and their reactions with various reagents are therefore not as difficult to follow as those of other sulphur compounds: furthermore, the total quantity of such compounds present in the distillates from various high-sulphur crude petroleum oils is relatively large. In fact, it has been estimated that if all of the mercaptans present in unrefined naphthas in this country alone could be recovered there would be available from 150 to 200 tons per day.[57] In spite of the knowledge of the chemistry of these compounds and the quantity available, few processes have been developed for their removal from petroleum distillates and their utilization. Practically all of the proposed operations consist of the sweetening of distillates, or the conversion of mercaptans to disulphides.

While it is unnecessary here to enter into a detailed discussion of the synthesis and chemical proporties of the mercaptans, some of their typical reactions will be mentioned.

The most general reaction employed in the synthesis of aliphatic mercaptans is that between potassium or sodium hydrosulphide and alkyl halides. The reaction of alcohols and phosphorus pentasulphide to yield mercaptans is applicable to both aromatic and aliphatic compounds, and with this same reagent phenols yield mercaptans or thiophenols, with the sulphur attached directly to the benzene nucleus. Distillation of a mixture of the alkali salts of sulphuric acid esters with alkali hydrosulphides also yields this same class of compounds. These methods of preparation may be represented by the following typical reactions:

$$\text{(a)}\quad C_2H_5Cl + KSH \longrightarrow C_2H_5SH + KCl$$

$$\text{(b)}\quad 5C_2H_5OH + P_2S_5 \longrightarrow 5C_2H_5SH + P_2O_5$$

$$\text{(c)}\quad 5C_6H_5OH + P_2S_5 \longrightarrow 5C_6H_5SH + P_2O_5$$

$$\text{(d)}\quad C_2H_5SO_4Na + NaHS \longrightarrow C_2H_5SH + Na_2SO_4$$

An interesting method for the preparation of tertiary mercaptans, particularly *ter*-butyl mercaptan, is by the interaction of sulphur and magnesium *ter*-butyl chloride in ether solution.[58] This mercaptan could not be separated from its ether solution by distillation. It was therefore precipitated as its mercury salt, and the latter decomposed with liquid hydrogen sulphide to yield mercuric sulphide and the free mercaptan.

With the exception of methyl mercaptan which is normally a gas, the aliphatic mercaptans are generally liquids possessing boiling points somewhat lower than the corresponding alcohols.[59] This difference of boiling point, however, becomes less as the number of carbon atoms in the molecule increases. For example, the boiling points of ethyl mercaptan and ethyl alcohol have been reported as 34.7° to 37° C. and 78.4° C., respectively, while the boiling points of n-heptyl mercaptan and the corresponding alcohol have been given as 174° to 175° C. and 175.8° C., respectively. In the aromatic series greater irregularities are encountered with respect to both boiling points and melting points, due no doubt to the effect of substituent groups. The specific gravities of aliphatic mercaptans are generally less than 1, ranging from about 0.83 to 0.89, while the aromatic mercaptans are usually heavier than water. The mercaptans of lower molecular weight possess disagreeable and unpleasant odors, while those of high molecular weight, such as myricyl mercaptan ($C_{30}H_{61}SH$), are odorless. Some aromatic mercaptans of fairly low molecular weight, such as o-xylene dimercaptan, have been described as odorless. Incidentally, because of its penetrating odor, volatility, and insolubility in water, ethyl mercaptan in concentrations of 4 grams per 1000 cubic feet of gas has been used for the detection of leaks in gas mains.[60]

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[57] Malisoff, Marks and Hess, "Study of Mercaptan Chemistry," *Chemical Reviews*, 1930, 7, 493. This is a critical presentation and discussion of the physical and chemical properties of mercaptans and contains an excellent bibliography.

[58] Rheinboldt, Mott and Motzkus, *J. pr. Chem.*, 1932, (3) 134, 257; *Chem. Abs.*, 1932, 26, 5544.

As the mercaptans contain an —SH group they may be considered as derivatives of hydrogen sulphide, or as alcohols in which the oxygen atom has been replaced by sulphur. As derivatives of hydrogen sulphide the mercaptans should be acidic in nature and some of their reactions bear this out. Just how acid the individual mercaptans are, and how they stand in relation to one another, apparently has not been determined on the basis of conductivity methods.[61] With alkalies, such as sodium or potassium hydroxides, or with metallic hydroxides, or oxides, the corresponding salts, or mercaptides, are formed. As these reactions are of particular interest in the sweetening operation they are more fully discussed later.

One of the characteristic reactions of mercaptans is that with oxidizing agents. With mild oxidizing agents, such as iodine, particularly under alkaline conditions, the mercaptans are converted to disulphides.[61a] This reaction has served for a quantitative estimation of mercaptans.[62] Reid and Sampey [63] have described two acidimetric methods for the determination of mercaptans (in benzene solutions). In the first method the hydrogen iodide formed in the oxidation of mercaptans with iodine is titrated; while in the second, the hydrogen chloride liberated by the action of mercuric chloride on the mercaptans is estimated. The latter reaction is given as:

$$RSH + HgCl_2 \longrightarrow RSHgCl + HCl$$

With chlorine or bromine, the mercaptans also yield disulphides, though side reactions take place at the same time with the formation of other products, such as sulphobromides, sulphones, and sulphonic acids. These reactions with halogens may be represented by:

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[59] For the preparation and physical properties of primary and secondary aliphatic mercaptans containing from one to nine carbon atoms, see Ellis and Reid, *J.A.C.S.*, 1932, **54**, 1674.

[60] Thau, *Gas- und Wasserfach,* 1931, **74**, 247; *Brit. Chem. Abs.* **B**, 1931, 467. For the use of mercaptans as odorizing materials see also Piotrowsky and Winkler, *Gas- und Wasserfach,* 1932, **75**, 262; *Brit. Chem. Abs.* **B**, 1932, 488; Harris, U. S. Patent 1,883,899, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 1067; Dobrovolny, U. S. Patent 1,905,817, April 25, 1933; *Chem. Abs.*, 1933, **27**, 3542; Sayers, Fieldner, Yant, Leitch and Pearce, *Bur. Mines Rept. of Investigations* 3007, 1930; *Chem. Abs.*, 1930, **24**, 3884.

[61] Malisoff, Marks and Hess, *loc. cit.*

[61a] For the oxidation of mercaptans with the sodium salt of iodoacetic acid ($2RSH + ICH_2COONa \rightarrow RSSR + CH_3COONa + HI$) in the presence of selenium, copper or arsenic, see Bersin and Logemann, *Ann.*, 1933, **505**, 1; *Chem. Abs.*, 1933, **27**, 5307.

[62] For the determination of mercaptans with iodine in acid solution, see Kimball, Kramer and Reid, *J.A.C.S.*, 1921, **43**, 1199.

[63] *J.A.C.S.*, 1932, **54**, 3404.

$$2C_2H_5SH + I_2 \longrightarrow 2HI + C_2H_5S.SC_2H_5$$
$$2C_2H_5SH + Br_2 \longrightarrow C_2H_5S.SC_2H_5 + 2HBr$$
$$2C_2H_5SH + 3Br_2 \longrightarrow 2C_2H_5Br + 2HBr + 2BrS$$
$$C_6H_5SH + Cl_2 \longrightarrow C_6H_5SCl + HCl$$

Other oxidizing agents which react with mercaptans to form disulphides are atmospheric oxygen, ferric chloride, ferricyanides, and sulphur. More energetic oxidizing agents, for example nitric acid, convert mercaptans into sulphonic acids.

$$2RSH + S \longrightarrow H_2S + RS.SR$$
$$2RSH + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + RS.SR$$
$$RSH + 2HNO_3 \longrightarrow RSO_3H + H_2O + 2NO$$

In carbon bisulphide solutions mercaptans react with sulphur monochloride to yield polysulphides,[64] for example:

$$2RSH + S_2Cl_2 \longrightarrow (RS)_2S_2 + 2HCl$$

Reaction with thionyl chloride leads to a mixture of disulphide and trisulphide,[65] thus:

$$4RSH + SOCl_2 \longrightarrow R_2S_2 + R_2S_3 + H_2O + 2HCl$$

The relation of mercaptans to alcohols is shown by the fact that mercaptans esterify organic acids just as alcohols do. The limits of esterification appear to be lower, however, with the mercaptans than with the corresponding alcohols.[66] The general reaction may be represented by

$$RCOOH + HSR \longrightarrow H_2O + RCOSR$$

The reactions of mercaptans with aldehydes[66a] to form mercaptals and with ketones to form mercaptoles appear to be characteristic.[66b] Some of the sulphones of the latter compounds have found use as soporifics; as for example sulphonal $(CH_3)_2C(SO_2C_2H_5)_2$, which is the sulphone of the mercaptole obtained by the reaction of acetone with ethyl mercaptan.[67] In this connection it may be mentioned also that carbohydrates similarly form condensation products with mercaptans; and that optically active amyl mercaptan, prepared from the corresponding alcohol, has been used in the resolution of racemic saccharides.[68]

One interesting point concerning the optical activity of some mercaptans is the reversal of rotation on oxidation. Thus Levene and Mikeska[69] have observed that oxidizing 2-mercaptoisohexane, $[\alpha]^{20}_{D} = +21.21°$, with nitric acid produced 2-isohexanesulphonic acid having $[\alpha]^{20}_{D} = -6.7°$. Also, 1,2-diphenylethyl mercaptan, $[\alpha]^{20}_{D} = +8.56°$, on oxidation yielded 1,2-diphenylethylsulphonic acid having $[\alpha]^{20}_{D} = -36.40°$. This reversal of rotation is similar to that observed by these same workers with other mercaptans[70] on oxidation and also resembles that accompanying the halogenation of secondary alcohols.[71]

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[64] Klason, *J. pr. Chem.*, 1877, (2) 15, 274.

[65] Holmberg, *Ann.*, 1908, **359**, 81.

[66] Sachs and Reid, *J.A.C.S.*, 1916, **38**, 2746; Kimball and Reid, *J.A.C.S.*, 1916, **38**, 2757; Faber and Reid, *J.A.C.S.*, 1917, **39**, 1930.

[66a] Addition products of mercaptans with aldehydes (formaldehyde) which are considered as intermediate compounds in the formation of mercaptals are described by Levi, *Gazz. chim. ital.*, 1932, **62**, 775; *Chem. Abs.*, 1933, **27**, 268.

[66b] This reaction has been proposed for the preparation of synthetic resins: British Celanese, Ltd., British Patent 367,759, 1929; *Chem. Abs.*, 1933, **27**, 2053.

[67] See also Chapter 34.

[68] Votocek and Vesely, *Ber.*, 1914, **47**, 1515; *Chem. Abs.*, 1914, **8**, 2716. For the preparation of the mercaptals of xylose and maltose, see Wolfrom, Newlin and Stahly, *J.A.C.S.*, 1931, **53**, 4379.

[69] *J. Biol. Chem.*, 1925, **65**, 515; *Brit. Chem. Abs.* **A**, 1926, 46.

[70] *J. Biol. Chem.*, 1924, **59**, 473; *Chem. Soc. Abs.*, 1924, **126** (1), 940.

[71] *J. Biol. Chem.*, 1925, **65**, 507; *Brit. Chem. Abs.* **A**, 1926, 45.

In addition to the uses already pointed out the bathochromic action of mercaptan groups in azo dyes might be mentioned, as the introduction of such a group often deepens the shade of the color.[72] Other types of dyes for which various mercaptans serve as intermediates are those of the anthraquinone series, thioindigos, and indamines. In addition the metallic salts of certain amino mercapto compounds, of mercapto acid esters, and of thioglucose have found some application in therapeutics. The synthesis of various mercapto compounds also appears to be of interest in the rubber field.[73]

The use of mercaptans as pickling inhibitors has been proposed by Calcott and Lee.[74] One of the chief disadvantages connected with the acid treatment of metals is that the free metal is attacked. Some substances which have been suggested as inhibitors of this solvent effect of the acid on the metal are sulphonated slaughterhouse waste and sludges from the sulphuric acid treatment of coal-tar and petroleum products. Both alkyl and aryl mercaptans possess this inhibiting effect to a marked degree, though their value varies with the kind and concentration of acid used, the temperature of the bath and the type of metal. The inhibiting action of some of the more common mercaptans on mild steel treated at 60° C. with 5 per cent sulphuric acid, containing 0.3 per cent mercaptan, was as follows:

	Inhibition Per Cent
Thiophenol	96.1
Thio-betanaphthol	93.1
Benzyl mercaptan	99.93
Isoamyl mercaptan	99.93
Isopropyl mercaptan	99.84

The inhibitor may be mixed with an acid dispersing agent such as Twitchell's reagent, Turkey red oil or sludge acids, or it may be dispersed in concentrated acids. If the inhibitor should decrease the rate of reaction to such an extent that the time for pickling is unduly prolonged, its action can be offset by the addition of a metallic chloride such as sodium chloride.

Derby and Cunningham[75] have reported that either aliphatic or aromatic mercaptans when heated to about 115° to 125° C. with phosphorus pentasulphide, or trisulphide, yield a product which is a clear syrupy liquid, and which, because of its collecting power, can be used in ore-flotation processes. Similar products can be obtained from the alkali ethoxides or phenoxides and phosphorus pentasulphide.

With the advent in the petroleum refinery of methods for the isolation of mixtures of the lower aliphatic mercaptans (methyl, ethyl, propyl or isopropyl) many other interesting applications will no doubt be found for compounds of this type.

Some of the reactions of mercaptans which have been described will be discussed in more detail, particularly those used in the extraction of such sulphur compounds from petroleum.

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[72] Reid and Waldron, *J.A.C.S.*, 1923, 45, 2399; Reid and Foster, *ibid.*, 1924, 46, 1936; Reid and Palmer, *ibid.*, 1925, 48, 528. Blumenstock-Halward and Jusa, *Monatsh.*, 1928, 50, 123; Blumenstock-Halward and Riess, *Monatsh.*, 1928, 50, 139; *Brit. Chem. Abs.* A, 1928, 1371.

[73] Malisoff. Marks and Hess, *loc. cit.*

[74] U. S. Patent 1,785,513, Dec. 16, 1930; assigned to E. I. duPont de Nemours & Co., Inc. Also, E. I. duPont de Nemours & Co., Inc., and Imperial Chemical Industries, Ltd., British Patent 346,992, 1932; *Chem. Abs.*, 1932, 26, 687.

[75] U. S. Patent 1,812,839, Jan. 30, 1931; *Brit. Chem. Abs.* B, 1932, 350.

Reaction of Mercaptans with Alkalies

In the refining of petroleum distillates, particularly from high sulphur crude oils, it is customary to wash them with solutions of sodium hydroxide before treating with sulphuric acid or before sweetening by the use of sodium plumbite solution. This alkali wash is given in order to eliminate the hydrogen sulphide dissolved in the distillate, as this substance is oxidized by the sulphuric acid with a corresponding loss of acid; or it reacts with the lead present in the plumbite solution to form lead sulphide, thereby resulting in an excessive consumption of lead.

Some mercaptans are extracted from the distillate by this alkaline wash as alkali salts or mercaptides. Complete extraction of mercaptans cannot be secured in this manner, except possibly of low-boiling ones, or when only a small proportion are present. This is due to the fact that alkali mercaptides, like the alkali sulphides, are readily hydrolyzed. The reaction therefore between alkali, in aqueous solution, and mercaptans can be represented by the reversible equation

$$\mathrm{RSH} + \mathrm{NaOH} \rightleftharpoons \mathrm{RSNa} + \mathrm{H_2O}$$

Alkaline extraction as a means of purification of naphtha likewise provides a method for the concentration of the lower mercaptans as their alkali mercaptides. From this alkaline extract the mercaptans themselves can be recovered by blowing with steam, yielding a mixture of ethyl and methyl mercaptan, sometimes with propyl or isopropyl mercaptan. In this way an alkaline washing liquor may be largely freed from sulphur. By blowing the liquor with air instead of steam, disulphides are formed.

Solutions of the lower-boiling mercaptans may be obtained in the following manner. Sour petroleum distillates, such as gasoline or kerosene, are treated with a 20 per cent aqueous solution of sodium hydroxide until the free alkali content of the solution has decreased to 10 per cent or less. This yields a solution containing both sodium mercaptides and sodium sulphide. Treatment of this solution with calcium hydroxide converts the sodium sulphide to sodium hydroxide and calcium sulphide is precipitated, which may then be separated. Spent lime solutions, composed largely of calcium hydrosulphide, may be used in place of calcium hydroxide.[76]

By extracting distillates containing mercaptans with sodium hydroxide solutions of different concentrations and then determining the distribution ratios, Meyer[77] obtained results which indicated that for the same weight of sodium hydroxide the more dilute solutions extracted the larger proportion of mercaptans. For the same strength of caustic soda solution, however, the quantity of mercaptans extracted was not proportional to the volume of solution used; thus, doubling the volume of caustic solution used did not double the quantity of mercaptans extracted. A countercurrent extraction using a series of pumps and settling tanks and enough caustic soda solution to remove the mercaptans gave better results than did batch treating. The efficiency of such a system was represented by $\frac{n}{n+1}$, in which n is the number of stages. The efficiency of a four-stage system, for example, would be 80 per cent. The mercaptans could be recovered by boiling the caustic solution.

Countercurrent extraction by caustic soda solution containing dissolved lead compounds, or by aqueous solutions of salts such as copper or magnesium chlorides, has been described by Peterkin.[78] Such solutions may be regenerated by blowing with a stream of air, or other oxygen-containing gas mixtures.

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[76] Wendt, U. S. Patent 1,791,179, Feb. 3, 1931; assigned to Standard Oil Company of Indiana; *Chem. Abs.*, 1931, **25**, 1667.

[77] *J. Inst. Pet. Tech.*, 1931, **17**, 621.

Vesselovsky and Kalichevsky[79] have reported that mercaptans can be extracted quantitatively from naphtha by sodium or potassium hydroxide dissolved in absolute alcohol. The reaction appears to be the formation of mercaptides and water, and the hydrolysis of the mercaptides in alcohol is extremely low.

When dissolved in petroleum distillates mercaptans not only react with aqueous and non-aqueous solutions of alkalies, but also with solid alkalies. Vesselovsky and Kalichevsky[80] observed that both solid sodium and potassium hydroxides extract mercaptans, sodium hydroxide reacting more rapidly than potassium hydroxide.

When mercaptans are added to liquid ammonia, slightly soluble ammonium mercaptides are formed.[81] These substances are white, crystalline bodies. On the addition of metallic sodium to a solution of these mercaptides in liquid ammonia a rapid reaction takes place with the formation of sodium mercaptide, ammonia and hydrogen.

$$RSH + NH_3 \longrightarrow RSNH_4$$
$$2RSNH_4 + 2Na \longrightarrow 2RSNa + 2NH_3 + H_2$$

Billheimer and Reid[82] observed that when the alkaline solutions of mercaptans are heated to temperatures of about 260° C., three simultaneous reactions take place: the formation of (1) alcohol, (2) thioethers, and (3) olefins. These may be represented by the following equations:

$$(1)\quad RSH + 2NaOH = ROH + Na_2S + H_2O$$
$$(2)\quad 2RSH + 2NaOH = R_2S + Na_2S + 2H_2O$$
$$(3)\quad RCH_2CH_2SH + 2NaOH = RCH{=}CH_2 + Na_2S + H_2O$$

Secondary mercaptans react to a greater degree than the primary; for example, when heated for 2 hours at 260° C. with $3N$ caustic solution 52.2 per cent of n-propyl mercaptan reacted with the alkali, while under the same conditions 65.4 per cent of isopropyl mercaptan reacted.

These reactions are also affected by the temperature as shown by the following results obtained with n-butyl mercaptan and $3N$ caustic solution on heating for 2 hours:

Temperature	250° C.	260° C.	270° C.
Per cent mercaptan reacting	30	49.6	63

When heated for 4 hours at 250° C. it was found that 47.2 per cent of the mercaptan reacted, thus indicating the favorable influence of time on the reaction.

The strength of the alkali also plays a very important part. As shown in Table 91, which gives the percentage decomposition of n-butyl mercaptan when heated for a period of 2 hours at 260° C. with sodium hydroxide solutions of various concentrations, the percentage of the mercaptan decomposed is greater with the more concentrated solutions, varying almost directly as the concentration. One curious fact noted by Billheimer and Reid is that thioethers constituted a much higher percentage of the decomposition products when dilute alkali was used than with the more concentrated solutions.

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[78] U. S. Patent 1,810,369, June 16, 1931; assigned to Atlantic Refining Co.; *Brit. Chem. Abs.* **B**, 1932, 412. *Cf.* Kimball, U. S. Patent 1,892,801, Jan. 3, 1933; *Chem. Abs.*, 1933, **27**, 2294.

[79] *Ind. Eng. Chem.*, 1931, **23**, 181.

[80] *Loc. cit.*

[81] Williams and Gebauer-Fuelnegg, *J.A.C.S.*, 1931, **53**, 352.

[82] *J.A.C.S.*, 1930, **52**, 4338.

TABLE 91.—*Decomposition of n-Butyl Mercaptan with Sodium Hydroxide at 260° C.*

Conc. of NaOH	0	0.1*N*	0.5*N*	1.0*N*	2*N*	3*N*
Per cent decomposed	0.0	2.1	9.8	20.2	33.8	49.6
R_2S formed	0.0	1.7	4.9	5.4	7.8	8.1
Per cent R_2S	—	81	50	27	28	16

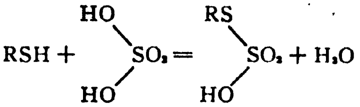
This "desulphydration" of mercaptans has been observed also with aralkyl mercaptans.[83] When α-phenylethyl-, β-phenylethyl-, or γ-phenylpropyl-thiols were heated to 230° C. with solid potassium hydroxide hydrogen sulphide was eliminated and the corresponding olefin obtained. A 53 per cent yield of the olefin was obtained from the β-phenylethylthiol, while very much lower yields were given by the other two thiols.

The sweetening of light sour distillates by countercurrent extraction with hot alkaline solutions has been proposed by Kimball.[84] In his process the aqueous alkaline solution is kept at a temperature which is high enough to maintain the distillate in the vapor phase. Evaporation of the alkaline solution may be prevented by the application of pressure. It is probable that the reactions taking place during this procedure are, at least in part, those described above.

ACTION OF SULPHURIC ACID ON MERCAPTANS

As sulphuric acid is almost universally employed in the refining of petroleum distillates its action upon mercaptans is of interest.

Erlenmeyer[85] was probably the first to show that mercaptans could be oxidized to the corresponding disulphides by the use of concentrated sulphuric acid. Wood, Lowy and Faragher[86] showed that by treating naphtha solutions of n- and iso-amyl mercaptans with concentrated sulphuric acid the mercaptans are oxidized to disulphides. They further reported that after treating these solutions of mercaptans with a relatively small quantity of sulphuric acid, the sulphur content increased. This increase in sulphur content was not observed on treating the naphtha alone with sulphuric acid. When the naphtha solutions were treated with large proportions of acid a decrease in sulphur content occurred, indicating that the disulphides were dissolved by the acid. Lowy and his collaborators suggest, therefore, that this increase in sulphur content may have been due to the formation of intermediate oxidation products, alkyl acid thiosulphates or dithiosulphates (equations 1 and 2 below), when the quantity of acid used was not sufficient for completely oxidizing the mercaptan to disulphide.



$$RSH + (HO)_2SO_2 = (RS)(HO)SO_2 + H_2O \qquad (1)$$

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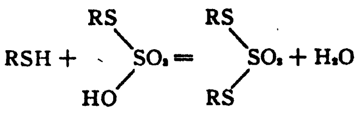
[83] Palfray, Sabetay and Sontag, *Compt. rend.*, 1932, **194**, 102; *Brit. Chem. Abs.* **A**, 1932, 266.

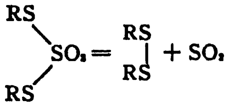
[84] U. S. Patent 1,831,916, Nov. 17, 1931; assigned to Shell Oil Co.; *Chem. Abs.*, 1932, **26**, 837. Also Kimball, British Patent 291,379, 1928; *Brit. Chem. Abs.* **B**, 1929, 843.

[85] *Jahresber.*, 1861, 690.

[86] *Ind. Eng. Chem.*, 1924, **16**, 1116.



(2)



(3)

Bennet and Story[87] concluded, from their study of the action of sulphuric acid on butyl mercaptan dissolved in gasoline, that not only was butyl disulphide and the corresponding sulphone ($C_4H_9S \cdot SO_2C_4H_9$) formed but also some elemental sulphur due to a side-reaction.

During the refining of certain light petroleum distillates with sulphuric acid Birch and Norris[88] observed that a small quantity of a substance was formed which was soluble in the distillate, insoluble in sulphuric acid, and corrosive to copper at the boiling point of the naphtha. The formation of this particular type of substance took place only when mercaptans were present in the untreated distillate. An investigation of various organic sulphides led to the conclusion that trisulphides were the cause of this corrosion. Diethyl trisulphide, $C_2H_5SSSC_2H_5$, synthesized from ethyl mercaptan and sulphur dichloride possessed the characteristic properties of the corrosive substance. Similar trisulphides were obtained by dissolving isobutyl or isoamyl mercaptans in naphtha and agitating with rock sulphur. Birch and Norris therefore consider that the formation of a polysulphide takes place, when sour crude distillates (i.e., distillates containing mercaptans) are treated with sulphuric acid, the reaction being represented by the equation:

$$2RSH + 2S \longrightarrow H_2S + R_2S_3$$

SWEETENING REACTION

By sweetening is generally meant the oxidation of mercaptans which are present in petroleum distillates, particularly gasoline and kerosene, to disulphides. One object of this process is improvement of odor, as the mercaptans, or at least those occurring in the petroleum distillates, possess very disagreeable odors, while the disulphides do not possess as unpleasant an odor and their presence in the distillates is not objectionable on this ground. Because, as previously mentioned, mercaptans are corrosive compounds and also catalysts for gum-formation, sweetening is almost imperative as a corrective measure in the manufacture of gasoline and kerosene. Any process which involves the actual removal or extraction of mercaptans, instead of their oxidation to disulphides, would, of course, yield a sweet oil.

Sweetening is usually accomplished by agitating the sour distillate with lead oxide dissolved in sodium hydroxide solution and then adding sulphur to precipitate the lead. Various modifications of this method are possible: for example, mixing a sufficient volume of oil containing dissolved sulphur with the sour oil and then agitating the mixture with the doctor solution; or agitating the sour distillate with the doctor solution, separating the aqueous layer, and adding

[87] *Oil and Gas J.*, 1927, 27 (48), 162; *Chem. Abs.*, 1927, 21, 2979.
[88] *Ind. Eng. Chem.*, 1929, 21, 1087.

a sufficient volume of oil containing dissolved sulphur to precipitate the lead.[89] Addition of solid sulphur to the sour oil after agitating with the doctor solution is also practiced.

The usual explanation [89a] of the reactions which take place during sweetening are: (1) reaction of the sour oil with the plumbite or doctor solution to form lead mercaptides which dissolve in the oil, imparting to it a yellow color; and (2) the subsequent formation of lead sulphide and disulphides on the addition of sulphur. The lead sulphide is insoluble in the oil and after precipitating is removed. The equations for these reactions are:

$$2RSH + Na_2PbO_2 = 2NaOH + Pb(SR)_2$$
$$Pb(SR)_2 + S = PbS + (RS)_2$$

This same procedure, agitation of the oil with doctor solution followed by the addition of sulphur, is the basis for the well-known doctor test.[89b] The formation of a precipitate on the addition of sulphur indicates a sour oil, while failure to form any precipitate indicates a sweet oil. It is customary before applying the doctor test to remove any hydrogen sulphide which may be present. This is necessary as hydrogen sulphide reacts immediately with the doctor solution to yield a precipitate of lead sulphide, and therefore interferes with the doctor test. Samples of sweet gasolines which have been stored for some time occasionally test sour, because of the formation of peroxides which react with the doctor solution to yield the insoluble lead peroxide.[90] Even turpentine, which contains no sulphur compounds, after exposure to air has shown a positive doctor test, because of the peroxides present. In applying the doctor test to stored samples, peroxides should therefore be eliminated by washing with solutions of alkalies (see Chapter 39) or by some other means.

While the reactions first mentioned are known to occur, there are other chemical changes which take place and the sweetening process is therefore much more complicated than these indicate. Wendt and Diggs [91] have shown that not only are mercaptans converted to disulphides by the oxidizing action of sulphur on their lead salts, but that the lead sulphide formed during sweetening is itself an active sweetening agent because of its property of absorbing mercaptans, thereby promoting their reaction with the doctor solution. Other sulphur compounds are absorbed at the same time. Wendt and Diggs have also pointed out that some distillates, such as pressure distillates, contain enough free or elemental sulphur to react with the lead mercaptides formed during the sweetening operation, and the addition of sulphur to such an oil is unnecessary.

Morrell and Faragher,[92] however, did not agree with this explanation of the use of lead sulphide. Instead they suggested that the lead sulphide is oxidized to lead sulphate by the air used for agitation, and that this lead sulphate then reacts with the sodium hydroxide to form sodium plumbite. From there on the usual sweetening reaction occurs. This they considered was indicated by the fact that a sample of sour commercial gasoline still gave a positive doctor test

[89] Chatfield, *Nat. Pet. News,* July 18, 1928, 56. Sturgis (*Oil and Gas J.,* 1933, 31 (45), 54; *Chem. Abs.,* 1933, 27, 3593) reports that gaseous hydrogen sulphide may be employed in place of elemental sulphur to precipitate the lead.

[89a] For a résumé of the theoretical principles involved as well as descriptions of batch and continuous processes of plumbite treatment, see Hallett and Sowers, *Petroleum Eng.,* 1930, 1 (8), 78; *Chem. Abs.,* 1930, 24, 3892.

[89b] For a comparison of the doctor and silver nitrate tests for mercaptans in gasolines see Mizuta, *J. Soc. Chem. Ind. Japan,* 1931, 34, 287; *Chem. Abs.,* 1931, 25, 5976. The estimation of mercaptans by the silver nitrate method is described by Borgstrom and Reid, *Ind. Eng. Chem., Anal. Ed.,* 1929, 1, 186; see also Chapter 50.

[90] Brooks, *Ind. Eng. Chem.,* 1924, 16, 588.

[91] *Ind. Eng. Chem.,* 1924, 16, 1113.

[92] *Ind. Eng. Chem.,* 1927, 19, 1045.

after 30 minutes agitation with air alone or in the presence of (1) sodium hydroxide, or (2) sodium hydroxide and lead sulphide. In the presence of lead sulphide, sulphur and sodium hydroxide (that is, all the ingredients required for sweetening) the sample was sweetened in 8 minutes and the alkaline solution then gave tests for a large proportion of sulphate ion. The reactions taking place can be represented in the following manner:

$$\begin{aligned} &PbS + 2O_2 \longrightarrow PbSO_4 \\ &PbSO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O \\ &2RSH + Na_2PbO_2 \longrightarrow 2NaOH + Pb(SR)_2 \\ &Pb(SR)_2 + S \longrightarrow PbS + (RS)_2 \end{aligned}$$

Other sulphides, such as those of silver, copper, mercury, and nickel, can be used instead of lead sulphide. When air is blown into suspensions of these sulphides in caustic soda solution, all are converted to the corresponding hydroxides, except mercury, which forms the oxide.

Lead sulphide as a sweetening reagent has been employed[93] with distillates in which the mercaptan content is so high that doctor sweetening becomes practically prohibitive on account of expense. The oil is agitated with caustic soda solution, sulphur, and a relatively small quantity of lead sulphide by blowing air through the mixture. In this way the mercaptans are said to be converted into less volatile polysulphides which remain in the still on subsequent redistillation. The temperature during redistillation should not exceed 160° C., to prevent decomposition of the polysulphides. Other heavy metallic sulphides can be used in place of lead sulphide.

Lachman,[94] on the other hand, believed that the interpretations given by Wendt and Diggs and by Morrell and Faragher are correct, because of the fact that both of the side reactions take place simultaneously. Confusion has arisen because gasolines are tested only to learn whether they are sweet or sour, and not quantitatively to determine how much mercaptan remains after each operation.

In studying the action of air on mercaptans in the presence of sodium hydroxide, Lachman used a 315 cc. flask in which were placed definite volumes of sodium hydroxide solutions of various concentrations and of sour gasoline. This left a definite volume of air remaining in the flask, which contained sufficient oxygen for the complete oxidation of the mercaptans. The flask and its contents were agitated at 20° to 25° C. for a definite period of time and the mercaptan content of the gasoline was determined. Some of the results obtained are given in Table 92.

These, and other results, clearly indicate that oxidation of mercaptans by air occurs in the presence of alkaline solutions. In some instances the mercaptans

TABLE 92.—*Effect of Air on Mercaptans in the Presence of Sodium Hydroxide.*
100 cc. of Gasoline; Mercaptan Content 0.0118*M*

Sodium Hydroxide		Air	Time	Mercaptan Oxidized
Cc.	Moles	Cc.	Hours	Per Cent
100	2	115	1 hour	68
100	2	115	2 “	72
100	2	115	4 “	95
50	2	165	1 “	53
50	2	165	5 “	92
50	2	165	7 “	96

[93] Standard Oil Development Co., British Patent 270,626, 1926; *Brit. Chem. Abs.* **B**, 1927, 931. See also, Fischer and Addems, U. S. Patent 1,789,335, Jan. 20, 1931; assigned to Standard Oil Development Co.; *Chcm. Abs.*, 1931, **25**, 1373. Fischer, U. S. Patent 1,795,278, March 3, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 1038.

[94] *Ind. Eng. Chem.*, 1931, **23**, 354.

were completely oxidized. The reactions taking place may be represented, according to Lachman, by the equations:

$$2RSH + O_2 = RSSR + H_2O_2$$
$$2RSH + H_2O_2 = RSSR + H_2O$$

The second reaction takes place very rapidly, and would be completed almost as soon as the primary reaction.

Lachman's data further indicated that the mercaptide ion, not the mercaptan, is actually oxidized, and that the rate of oxidation is governed by, the speed of diffusion of atmospheric oxygen into the alkaline layer. If the rate of oxidation is determined by the alkaline film and its oxygen content then this rate would be increased by increasing (1) the air pressure, (2) the area of the film by agitation, and (3) the surface of contact by the addition of finely divided solids. The second inference was verified by using very small quantities (1 cc.) of sodium hydroxide solution and agitating with sour gasoline in the presence of air as described above. The third inference was also verified by the addition of various catalysts, such as lead, cadmium, and zinc sulphides, barium sulphate and others, to the alkaline solution. The effects of such catalysts are shown in Table 93.

TABLE 93.—*Effect of Catalysts on Rate of Oxidation of Mercaptans.*
100 cc. of Gasoline; Mercaptan 0.0118*M*; 25 cc. of
2*M* NaOH + Catalyst; Air Volume 190 cc.

Catalyst	Mol.	Time	Mercaptan Oxidized Per Cent
Cadmium sulphide	0.001	1 hour	sweet
Zinc sulphide	0.001	1 "	87
Lead sulphide	0.0005	15 minutes	99+
Barium sulphate	0.002	20 "	58
Sulphur	0.03	10 "	sweet
None	—	1 hour	43

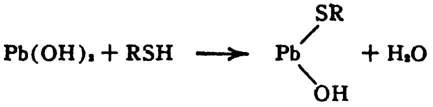
In other experiments it was found that lead sulphide was changed to lead oxide, and therefore one equivalent of litharge during the course of the reaction would react with more than two equivalents of mercaptans. Further, the presence of any sodium sulphide which might be formed during the sweetening process is detrimental only because in being converted to sodium thiosulphate it competes with the mercaptans for both free oxygen and sulphur.

NEUTRAL AND BASIC LEAD MERCAPTIDES

Ott and Reid[95] have found differences in the reactions between primary and secondary mercaptans with the doctor solution, and also in the subsequent reactions between the lead mercaptides thus formed and elemental sulphur.

When solutions of mercaptans in benzene are agitated with sodium plumbite solution two reactions are possible, (1) formation of neutral lead mercaptide, and (2) formation of basic lead mercaptide.

(1) $Pb(OH)_2 + 2RSH \longrightarrow Pb(SR)_2 + 2H_2O$

(2) 

$$Pb(OH)_2 + RSH \longrightarrow Pb\begin{matrix} \diagup SR \\ \diagdown OH \end{matrix} + H_2O$$

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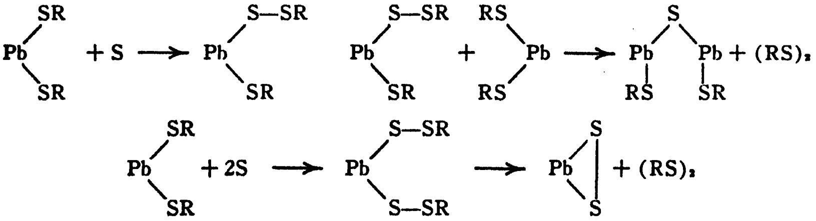
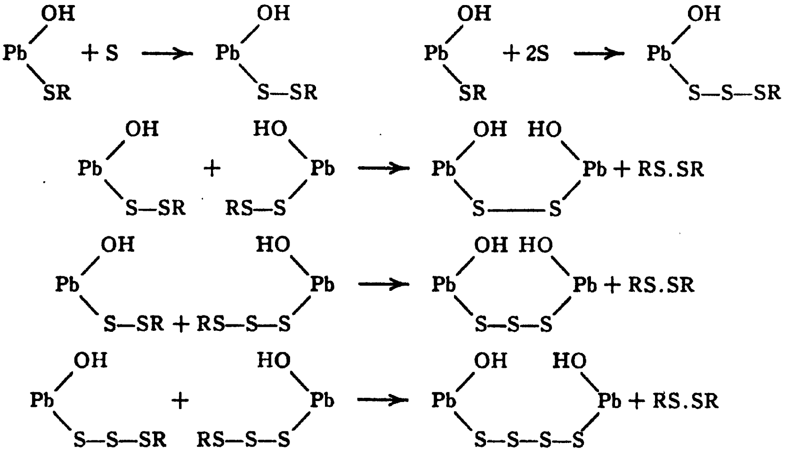
[95] *Ind. Eng. Chem.*, 1930, 22, 878, 884

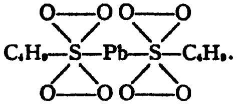
While both types of mercaptides are formed in all cases, the following generalizations appear to hold: the primary mercaptans form principally neutral lead mercaptides, the secondary mercaptans tend to form large quantities of the basic lead mercaptides, and the more concentrated the sodium plumbite solution the greater is the quantity of basic lead mercaptides in both instances.

The addition of sulphur to solutions of lead mercaptides does not, therefore, always lead to the formation of lead sulphide, as has been generally assumed. The addition of sulphur to solutions of neutral lead mercaptides usually results in the formation of a precipitate consisting of a mixture of lead-sulphide and the neutral lead mercaptide. It was reported that in one instance lead disulphide was formed. Reactions whereby such products could be formed might be represented in the following manner:



The addition of sulphur to solutions of basic lead mercaptides results in formation of precipitates which analysis shows to be mixtures of lead sulphide, lead hydroxide and sulphur.[96] In some instances—from the basic lead mercaptide of *sec*-butyl mercaptan, for example—compounds of the type $Pb_2(OH)_2S_3$ and $Pb_2(OH)_2S_4$ were obtained. The formation of such compounds may take place according to the following reactions:



When solutions of lead mercaptides are exposed to the air fairly stable peroxides of high, though varying, oxygen content are formed, which are insoluble in organic solvents.[97] They are also produced by the action of hydrogen peroxide on solutions of the mercaptides. From the lead mercaptide of *sec*-butyl mercaptan the peroxide, $Pb(SC_4H_9)_2O_8$, was obtained. As all tests failed to indicate that any of the oxygen was attached to the lead it was assumed that the constitution of the compound could be represented by  Peroxides of smaller oxygen content were also obtained from this same lead mercaptide. Light appeared to accelerate the formation of the peroxides.

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[96] Duncan and Ott (*J.A.C.S.*, 1932, 54, 4463) report that the basic lead derivatives of secondary butyl mercaptan (in benzene) react with sulphur to yield a mixture of basic lead polysulphides. No definite compounds could be isolated.

OTHER METHODS OF SWEETENING

Instead of adding sulphur to the sour oil after agitation with the doctor solution Hunn[98] suggested the addition of low molecular weight disulphides such as methyl or propyl disulphide. On standing, the lead is precipitated and a sweet oil obtained. Analysis of the precipitate formed from methyl disulphide indicated it to be lead methyl mercaptide.

For use in place of a solution of lead oxide Cannon and Gary[99] have suggested employing a solid reagent consisting of calcium hydroxide, lead oxide and sulphur. After mixing this reagent with the sour oil the mixture is filtered and a sweet oil obtained. The solid reagent, after the addition of sulphur, can be used again.

A modification of this process consists in first adding a small quantity of sulphur to the gasoline and then treating it with a mixture consisting of sodium hydroxide, calcium hydroxide, lead oxide, diatomaceous earth, and enough water to form a coherent mass.[100]

Brucite, or magnesium hydroxide, has been used as a sweetening agent. In this case elemental sulphur equivalent to that required for the oxidation of the mercaptans to disulphides is added to the sour distillate, and the distillate is then agitated with solid brucite.[101]

Other methods for sweetening petroleum distillates have been suggested. Lachman[101a] found that gasoline could be made sweet by agitating it with air in the presence of alkaline solutions containing finely divided carbon in suspension. Zurcher[101b] passed hydrocarbon vapors at 400° to 600° C. through activated carbon, the velocity of the vapors being rapid enough to avoid cracking. Malisoff[101c] treated oils containing mercaptans with solutions of an alkali metal hydroxide in methyl alcohol, sufficient water being added to the alcoholic solution to render it immiscible with the oil. Black and McConnell[101d] recommended aqueous solutions of alkalies with suspended manganese dioxide as contact agents. Exposure of sour distillates, after treatment with plumbite solution, to ultraviolet light results in the precipitation of the mercaptides.[101e] The oxidation of mercaptans by air is accelerated by x-rays.[101f] Solid sodium hydroxide has been used to give a negative doctor test to gasolines.[101g] Moser[101h] reported that a sweet but corrosive product was obtained when dry sodium hydroxide, or powdered sodium carbonate, and free sulphur were employed. The use of phosphorus pentoxide as a sweetening agent has also been proposed.[101i]

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[97] Ott and Reid, *Ind. Eng. Chem.*, 1930, 22, 882.

[98] U. S. Patent 1,786,246, Dec. 23, 1930; assigned to Standard Oil Development Co.

[99] U. S. Patents 1,789,167 and 1,789,168, Jan. 13, 1931; *Chem. Abs.*, 1931, 25, 1067; U. S. Patent 1,907,150, May 2, 1933; *Chem. Abs.*, 1933, 27, 3600. Cannon, U. S. Patent 1,888,219, Nov. 22, 1932; *Chem. Abs.*, 1933, 27, 1502; British Patent 367,969, 1930; *Chem. Abs.*, 1933, 27, 2294. All patents assigned to Cannon-Prutzman Treating Processes, Ltd.

[100] Cannon, U. S. Patent 1,798,784, March 31, 1931; assigned to Cannon-Prutzman Treating Process, Ltd. *Cf.* Hirt, U. S. Patent 1,910,288, May 23, 1933; *Chem. Abs.*, 1933, 27, 4070.

[101] Gardner and Higgins, *loc. cit.*

[101a] U. S. Patent 1,890,516, Dec. 13, 1932; assigned to Richfield Oil Co. of California; *Brit. Chem. Abs.* B, 1933, 740. See also I. G. Farbenindustrie A.-G., French Patent 741,890, 1933; *Chem. Abs.*, 1933, 27, 3481.

[101b] U. S. Patent 1,884,495, Oct. 25, 1933; assigned to Continental Oil Co.; *Chem. Abs.*, 1933, 27, 1158.

[101c] Canadian Patent 333,899, 1933; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1933, 27, 4916.

[101d] U. S. Patent 1,759,730, May 20, 1933; assigned to Richfield Oil Co. of California; *Chem. Abs.*, 1930, 24, 3638.

The use of hypochlorite solutions as sweetening agents in place of the doctor solution and sulphur has also been proposed. Thus Dunstan[102] sweetened a sour distillate by first removing hydrogen sulphide and then treating with a dilute solution of hypochlorous acid. Later the product is refluxed with slacked lime to hydrolyze any chlorinated compounds which might have been formed. Birch and Norris,[103] however, used an alkaline hypochlorite solution for the sweetening operation with cracked distillates. With this reagent hydrogen sulphide is oxidized to elemental sulphur and a small proportion of sulphuric acid, sulphides are oxidized to neutral sulphones, and mercaptans first to disulphides and then to sulphonic acids. As the oxidizing effect of the hypochlorite solution decreases with increasing alkalinity it is possible to adjust the alkalinity so that mercaptans are oxidized only to disulphides. Oxidation of mercaptans is also effected by chlorous acid in the presence of hydrochloric acid.[103a]

Demoulins and Garner[104] suggested the vapor-phase sweetening of petroleum distillates by treating the vapors with atomized hypochlorite solution.

COPPER MERCAPTIDES

Although the sweetening of sour oils is accomplished usually by the use of the sodium plumbite and sulphur, or some modification such as lead sulphide, caustic and air, or by the use of hypochlorite solutions, the employment of copper[105] salts has also been suggested. To effect this reaction, the sour oil is agitated with a water solution of a cupric salt, usually cupric sulphate, to which enough ammonia has been added to form the blue solution of ammonio-cupric sulphate. Light yellow cupric mercaptides are formed which are soluble in the oil. Addition of sulphur then precipitates cupric sulphide, yielding a sweet oil.[105a] Von Fuchs[105b] suggested agitation of the sour distillate with finely divided copper or cuprous oxide in the presence of a trace of ammonia, hydrogen chloride or sulphur dioxide.

[101e] Morrell, U. S. Patent 1,904,382, Apr. 18, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 3601.

[101f] Mekler, U. S. Patent 1,897,617, Feb. 14, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 2797.

[101g] Shumovski, *Grosnenskii Neftyanik*, 1932, **2** (No. 5-6), 59; *Brit. Chem. Abs.* **B**, 1933, 99.

[101h] *Petroleum Z.*, 1933, **29** (7), 5; *Chem. Abs.*, 1933, **27**, 3594.

[101i] Malishev, U. S. Patent 1,914,953, June 20, 1933; assigned to Shell Development Co.; *Chem. Abs.*, 1933, **27**, 4390.

[102] U. S. Patent 1,492.969, May 6, 1924; *Chem. Abs.*, 1924, **18**, 2072; British Patent 364,202, 1930; *Brit. Chem. Abs.* **B**, 1932, 249; British Patent 378,010, 1932; *Chem. Abs.*, 1933, **27**, 4067; all patents assigned to Anglo-Persian Oil Co., Ltd., *Oil and Gas J.*, 1928, **27** (30), 138. See also Thole and Card, U. S. Patent 1,776,340, Sept. 23, 1930; assigned to Anglo-Persian Oil Co., Ltd.; *Chem. Abs.*, 1930, **24**, 5476.

[103] *Refiner*, 1928, 7, No. 7, 94; *Chem. Abs.*, 1929, **23**, 1742. See also Birch, *Oil and Gas J.*, 1929, **28**, No. 1, 190; No. 2, 38; and Dunstan and Thole, *Oil and Gas J.*, 1929, **28**, No. 1, 190.

[103a] Taylor, U. S. Patent 1,908,273, May 9, 1933; assigned to Mathieson Alkali Works; *Chem. Abs.*, 1933, **27**, 3810.

[104] British Patent 216,918, 1923; *J.S.C.I.*, 1924, **43**, 665B.

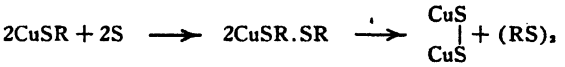
[105] Ziser and Osmer, U. S. Patent 1,784.215, Dec. 9, 1930; assigned to Standard Oil Co. of California. Hounsell, *Oil and Gas J.*, 1929, **27** (43), 31; *Chem. Abs.*, 1929, **23**, 3336.

[105a] For a similar use of ammonio-cadmium nitrate or chloride, see Culmer, U. S. Patent 1,899.314, Feb. 28, 1933; assigned to Lincoln Oil Refining Co.; *Chem. Abs.*, 1933, **27**, 3066. Morrell (U. S. Patent 1,911,640, May 30, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 4067) suggested a mixture of a copper salt, an alkali metal hydroxide and a solid adsorbent as a sweetening agent.

[105b] *Petroleum Z.*, 1933, **29**, 5; *Chem. Abs.*, 1933, **27**, 3592.

Duncan, Ott and Reid[106] have shown that when a dilute (0.3*N*) aqueous solution of cupric acetate is agitated with a dilute solution of a mercaptan in benzene insoluble cuprous mercaptide is immediately formed. These cuprous mercaptides react slowly with sulphur to yield insoluble copper sulphide, the analysis of which indicated it to be cupric sulphide, but which from its formation should be cuprous sulphide. The reactions with copper acetate, therefore, may be represented by:

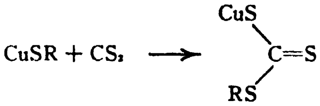
$$2Cu(C_2H_3O_2)_2 + 4RSH \longrightarrow 2CuSR + 4HC_2H_3O_2 + (RS)_2$$



$$2CuSR + 2S \longrightarrow 2CuSR.SR \longrightarrow \begin{matrix} CuS \\ | \\ CuS \end{matrix} + (RS)_2$$

The copper mercaptides obtained by the above method were all insoluble in water and in alcohol; those from normal mercaptans and from isopropyl and secondary butyl mercaptans were insoluble in ether and benzene, while the mercaptides from the higher secondary mercaptans were soluble. Light caused the derivatives of the secondary mercaptans to darken in color but did not affect those of the primary mercaptans. No basic copper mercaptides similar to the basic lead mercaptides were obtained.

Cuprous mercaptides also react readily with carbon disulphide to yield reddish thiocarbonates, which are much more soluble in benzene-carbon disulphide mixtures than the parent mercaptides are in benzene. The chemical properties of these thiocarbonates indicate very clearly that they are produced according to the reaction:



The benzene solutions of the cuprous derivatives of n-amyl and higher mercaptans often form jellies on standing, a change less likely to occur with the derivatives of secondary mercaptans.

ADSORPTION OF MERCAPTANS BY METALLIC SULPHIDES AND OTHER SUBSTANCES

As pointed out above, lead sulphide appears to have the property of adsorbing mercaptans from sour gasolines. In addition to lead sulphide, other sulphides, such as those of copper, tin, cadmium and arsenic, have been shown to possess the same property.[107]

Slagle and Reid[108] have investigated the adsorption of normal mercaptans, ranging from methyl to nonyl, from benzene solutions by cupric sulphide and other adsorption agents. The sulphides of copper and other metals were found to be adsorbents for normal mercaptans, though the proportion of mercaptan adsorbed varied widely with the different sulphides. Cupric compounds in general were good adsorbents, basic cupric carbonate being the best. Some of the results of duplicate experiments made by these investigators, using 50 cc. of a solution of n-butyl mercaptan (corresponding to 0.5 per cent sulphur by weight) and 0.5 gram of adsorbent, are given in Table 94.

[106] *Ind. Eng. Chem.*, 1931, 23, 381.
[107] Greer, *Ind. Eng. Chem.*, 1929, 21, 1033.
[108] *Ind. Eng. Chem.*, 1932, 24, 448.

TABLE 94.—*Removal of n-Butyl Mercaptan from Benzene.*

Adsorbent	Mercaptan Removed —Per Cent—	
Basic cupric carbonate	99.8	100
Cupric hydroxide	99.8	99.9
Cupric sulphide	65.0	66.0
Copper (precipitated powder)	50.1	50.6
Mercuric sulphide (black)	28.4	25.0
Lead sulphide	25.8	27.2
Antimony sulphide (red)	13.3	14.5
Cadmium sulphide	10.0	10.0
Barium hydroxide	5.4	5.4
Silica gel, activated	1.0	1.1
Antimony sulphide (black)	1.0	0.0
Iron powder	0.1	0.4
Kieselguhr	0.0	0.0

It was also determined that the percentage of mercaptan removed from solution depended upon (1) the concentration of the mercaptan in solution, and (2) the proportion of cupric sulphide used. One surprising result was that a single treatment with cupric sulphide removed only slightly less mercaptan than when the same weight of sulphide was used but applied in four successive treatments. Later in the investigation it was found that a large portion of the primary mercaptans "removed" had been converted to disulphides, which may offer an explanation of these results.

In attempting to remove secondary mercaptans from solution by means of copper or cupric sulphide it was observed that a part of the copper was dissolved with the formation of cuprous mercaptides, and at the same time some disulphides were formed. This was especially true for secondary mercaptans containing five to eight carbon atoms per molecule. This reaction was noticed because of the change in color of the benzene solution, as the cuprous mercaptides from secondary mercaptans are soluble in that solvent. If the same reactions took place with normal mercaptans, the insoluble cuprous mercaptides would remain on the surface of the cupric sulphide without affecting the color of the benzene solution.

Low[109] suggested the use of lead sulphide in the refining of gasoline. The liquid is passed through a bed of the finely ground, dried sulphide. The lead sulphide is regenerated intermittently by treating with aqueous solutions of an alkali sulphide and drying at 230° F.

EFFECT OF OTHER REAGENTS ON MERCAPTANS

The effect of solutions, or suspensions, of a number of metallic salts and oxides on mercaptans dissolved in naphtha has been investigated by Borgstrom, Deitz and Reid.[110] The mercaptans used in this work varied from ethyl to amyl, and included both the primary and secondary. Copper acetate, mercuric acetate, and ammoniacal cupric sulphate all yielded sweet naphthas. With the first two salts there was actual removal of mercaptans from solution, while the last named effected oxidation of the mercaptan to disulphide.[111] With reagents such as mercuric oxide, copper oxide, and copper sulphate, which apparently form insoluble mercaptides, variable results were obtained. The acetates of sodium, calcium, barium, cobalt, zinc and iron produced little or no effect. Bismuth nitrate solution exhibited a greater degree of reactivity which may have been due to the nitric acid required in the preparation of the solution. Both neutral and acid solutions of cadmium chloride produced slight decreases in the mercaptan content of the naphthas. Sodium zincate solution, corresponding to the sodium plumbite solution, reacted to a greater extent with the lower mercaptans than with the higher. Sodium hydroxide completely removed the lower-boiling mercaptans, but less completely the higher-boiling ones. Increasing the concentration of the alkaline solution did not increase the solubility of the mercaptans.

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[109] U. S. Patent 1,777,619, Oct. 7, 1930; assigned to Richfield Oil Co. of California; *Chem. Abs.*, 1930, 24, 6001.

[110] *Ind. Eng. Chem.*, 1930, 22, 245.

[111] The removal of mercaptans, or other sour sulphur compounds, from cracked distillates has been described also by Gray, U. S. Patent 1,825,861, Oct. 6, 1931; assigned to Gray Process Corp.; Morrell, U. S. Patent 1,827,537, Oct. 13, 1931; assigned to Universal Oil Products Co.; *Brit. Chem. Abs.* B, 1932, 714.

In continuing the work with metallic salts a single sample of naphtha was used for making solutions of fourteen different mercaptans, normal and secondary from propyl to nonyl, and these solutions were treated with all the inorganic reagents which gave promise of a sweetening reaction.[112] The reagents were principally copper salts although three oxidizing agents, potassium permanganate, potassium dichromate, and potassium ferricyanide, were included. Of all the reagents only mercuric acetate yielded a sweet naphtha.

The steam distillation of naphtha, containing mercaptans volatile with steam, in the absence or presence of caustic soda solutions, did not appreciably lower the mercaptan content. Solutions of cupric sulphate or cupric acetate reduce the mercaptan content in proportion to the quantity of the salt employed.[113]

Various naphthas, having wide differences in boiling ranges and gravities, and to which mercaptans had been added, were steam distilled in the presence of solutions of copper salts alone or copper salts and sodium hydroxide.[114] Although some of the distillates were sweetened they still contained sulphur,—in some instances as much as 60 per cent of the added sulphur, part of which was in the form of disulphide.

The use of various salts, particularly cupric sulphate, as refining agents was discussed by Kalichevsky and Stagner.[115]

RECOVERY OF MERCAPTANS FROM PETROLEUM DISTILLATES

As previously pointed out there are very few methods for the actual recovery of mercaptans as such from petroleum distillates. Washing the distillate with sodium hydroxide solution does not extract all, as only part of the higher-boiling mercaptans are removed. Wendt[116] suggested the use of an alcoholic solution of sodium plumbite as a means of removing mercaptans, while Vesselovsky and Kalichevsky[116a] used alcoholic solutions of sodium or potassium hydroxide.

In recovering the mercaptides from the caustic soda solutions used in washing sour distillates, it is, of course, possible to liberate the free mercaptans by the addition of an acid. This method, however, also liberates hydrogen sulphide along with the mercaptans. Birch and Norris[117] took advantage of the fact that the mercaptans are weaker acids than hydrogen sulphide and that their salts are more easily hydrolyzed to obtain the mercaptans, free of hydrogen sulphide, by distillation of spent caustic soda solution. Along with the mercaptans disulphides also come over.

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[112] Borgstrom, *Ind. Eng. Chem.*, 1930, **22**, 250.
[113] Borgstrom, Roseman and Reid, *Ind. Eng. Chem.*, 1930, **22**, 248.
[114] Borgstrom and McIntire, *Ind. Eng. Chem.*, 1930, **22**, 253.
[115] "Chemical Refining of Petroleum," The Chemical Catalog Co., Inc., New York, 1933.
[116] U. S. Patent 1,658,505, Feb. 7, 1928; *Chem. Abs.*, 1928, **22**, 1233.
[116a] *Loc. cit.*
[117] *J.C.S.*, 1925, **127**, 898.

On the distillation of the spent caustic soda solution, used in washing a fraction representing the first 36 per cent (by volume) of a Persian crude oil, a mixture of mercaptans and disulphides was obtained. By washing this mixture with potassium hydroxide solution separation of these two classes of compounds was effected. Acidifying the potassium hydroxide solution liberated the free crude mercaptans. These crude mercaptans consisted of 55 to 60 per cent isopropyl mercaptan, 18 per cent isobutyl mercaptan, about 9 per cent of ethyl mercaptan, the intermediate fractions and a high-boiling residue accounting for the remainder. From the mixture of disulphides, obtained after separation of the mercaptans with potassium hydroxide, diethyl, diisopropyl and diisobutyl disulphides were isolated. In order to show the presence of these disulphides in the corresponding fractions it was necessary first to reduce them to the mercaptans (by means of zinc dust and glacial acetic acid) and to identify these.

As disulphides are insoluble in caustic soda solutions their presence along with mercaptans is explained in the following manner: The distillate used contained, in addition to mercaptans, both hydrogen sulphide and elemental sulphur. When this distillate was washed with caustic soda solution some sodium polysulphide was formed and remained in the aqueous layer, giving it a deep yellow color. On distillation of the spent caustic soda solution the sodium mercaptides reacted with the polysulphides to yield disulphides.[118]

The reclaiming of spent sodium hydroxide solutions by removing the sulphur compounds in the form of mercaptans, mercaptals, sulphides or disulphides, has been described by Mendius.[119] This is accomplished by the countercurrent scrubbing of the alkali solution with steam or with a dry sulphur-free gas.

It is interesting to note that phenolic substances may be obtained from spent doctor solutions.[119a] On acidifying the alkaline liquid with hydrogen sulphide (or sulphuric acid), an oily layer separates. This is distilled and the fraction boiling between 180° and 270° C. is treated with a reducing agent (e.g., iron and sulphuric acid) to convert the disulphides present to mercaptans. The oily material is then separated (by distillation) into two fractions which boil at 180° to 220° C. and 220° to 270° C., respectively, and these are subsequently oxidized with air, to change any mercaptans remaining to disulphides. After oxidation the fractions are again subjected to fractional distillation and phenols, practically free of disulphides, are said to be obtained.

Ferber[120] reported that the complete removal of sulphur compounds from the heavier distillates (transformer oils) can be effected by treatment with metallic sodium. The carbonaceous residue thus obtained, after acidifying with dilute hydrochloric acid followed by extraction with light petroleum ether and evaporation of the solvent, yielded a light yellow oil. This proved to be a mixture of disulphides from which, after reduction, amyl, heptyl and octyl mercaptans were obtained.

DISULPHIDES

While sulphur compounds of this type are known to exist in petroleum distillates, their actual isolation and utilization apparently have not been investigated, no doubt because they are very easily removed, together with other sulphur compounds, from the various distillates by treatment with sulphuric acid.[121] As pointed out in the discussion of the sweetening reaction, these sulphur compounds possess less disagreeable odors than the corresponding mercaptans which consequently are converted to disulphides in order to improve the odor of the lower-boiling distillates, such as gasoline or kerosene.

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[118] For the reaction of sulphur and sodium ethylmercaptide, see Böttger, *Ann.*, 1884, 223, 348. For the reaction of alkalimercaptides and sodium polysulphides, see Holmberg, *Ann.*, 1908, 359, 81.

[119] *Refiner*, 1932, 11, 370.

[119a] Berry, Melvill and Banks, British Patent 386,977, 1933; *Chem. Abs.*, 1933, 27, 4665.

[120] *Z. angew. Chem.*, 1928, 41, 680; *Chem. Abs.*, 1928, 22, 4237.

The disulphides can, of course, be obtained from petroleum by indirect methods. For instance, Birch and Norris[117] in the extraction of mercaptans from light sour distillates obtained not only mercaptans but also disulphides, the latter being formed in secondary reactions taking place when the distillate was washed with caustic soda solutions. The mercaptans so obtained could also have been oxidized in alkaline solutions to disulphides. Ferber[122] also reported obtaining disulphides from the heavier distillates by the use of metallic sodium.

The relation between disulphides and mercaptans has been repeatedly pointed out, the former being an oxidation product of the latter. Disulphides, too, may be easily reduced to mercaptans.[122a] These relations can be represented by:

$$4RSH + O_2 \longrightarrow 2H_2O + 2RS.SR$$
$$RS.SR + H_2 \longrightarrow 2RSH$$

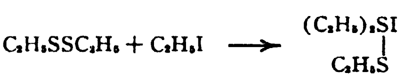
Wiezevich, Turner and Frolich[123] reported that ethyl mercaptan, at about 100° C., may be oxidized with air in the presence of iron, copper, iron sulphide or charcoal. Approximately 90 per cent yields of ethyl disulphide are said to be obtained under these conditions.

Using ethyl disulphide as an example, other typical reactions of disulphides are as follows: With dilute nitric acid this substance yields the compound $C_2H_5SO_2 \cdot SC_2H_5$. On reduction with zinc and dilute sulphuric acid this substance yields, first, the disulphide and, second, ethyl mercaptan. When dissolved in alcohol and reduced with zinc alone, zinc ethyl mercaptan and the zinc salt of ethylsulphuric acid are obtained:[124]

$$2C_2H_5SO_2SC_2H_5 + 2Zn \longrightarrow (C_2H_5S)_2Zn + (C_2H_5SO_2)_2Zn$$

When dissolved in alcohol and treated with sulphur, particularly in the presence of ammonia, a tetrasulphide $(C_2H_5)_2S_4$ is formed.[125]

The disulphides also react very slowly with alkyl halides, especially the iodides, to yield sulphonium compounds. A typical reaction would be:



$$C_2H_5SSC_2H_5 + C_2H_5I \longrightarrow \begin{array}{c}(C_2H_5)_2SI\\ |\\ C_2H_5S\end{array}$$

Such reactions are extremely slow but may be accelerated if carried out in the presence of mercuric iodide.[126] In this case, however, the free sulphonium iodide is not obtained but rather its double compound with mercuric iodide, as for example $(C_2H_5)_3S_2I \cdot 2HgI_2$.

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[121] Wood, Lowy and Faragher, *Ind. Eng. Chem.*, 1924, **16**, 1116; Wood, Sheely and Trusty, *Ind. Eng. Chem.*, 1926, **18**, 169; Wright, *J. Inst. Pet. Tech.*, 1929, **15**, 214.

[122] *Loc. cit.*

[122a] For the application of this reaction to the refining of gasoline-containing distillates, see Morrell, U. S. Patent 1,920,270, Aug. 1, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 4918. Also French Patent 736,834, 1932; *Chem. Abs.*, 1933, **27**, 1499.

[123] *Ind. Eng. Chem.*, 1933, **25**, 295.

[124] Earlier workers considered that two oxidation products were obtained, a disulphoxide, $C_2H_5SO \cdot OSC_2H_5$, and the ethyl ester of ethylthiosulphonic acid, $C_2H_5SO_2 \cdot SC_2H_5$. The latter formula appears to be the more generally accepted. See Saizew and Lukaschweitz, *Z. für Chemie*, 1868, 641; Pauly and Otto, *Ber.*, 1878, **11**, 2073; Hinsberg, *Ber.*, 1908, **41**, 2836, 4294; Smiles and Gibson, *J.C.S.*, 1924, **125**, 176; Miller and Smiles, *J.C.S.*, 1925, **127**, 224.

[125] Holmberg, *Ber.*, 1910, **43**, 222.

[126] Hilditch and Smiles, *J.C.S.*, 1907, **91**, 1394.

As the disulphides possess boiling points much higher than the corresponding mercaptans and less disagreeable odors, there is the possibility of their use as solvents. Ethyl disulphide, for example, has been mentioned as a solvent for rubber, as well as for resins produced from xylenol and sulphur monochloride.[127]

ORGANIC SULPHUR COMPOUNDS

In addition to the mercaptans which appear in the various distillates from petroleum crude oils, particularly from high sulphur crudes, a large number of different sulphur compounds have been isolated. The particular types of compounds differ with the locality from which the crude oil is obtained. Such an immense amount of work has been done on the isolation of these compounds, that it is only possible to give a very brief review of some of it.[128]

THIOETHERS

Mabery and Smith[129] showed the presence of thioethers in petroleum in the following manner: The fraction of an Ohio crude oil boiling between 200° and 300° C. was extracted with concentrated sulphuric acid and the acid extract neutralized with lead carbonate or calcium hydroxide. On evaporation a salt separated which was then mixed with water and steam-distilled. A light yellow oil was obtained, and the portion of this boiling between 80° and 190° C. was fractionated at 100 mm. The fraction boiling from 80° to 90° C. contained no sulphur compounds, but the other fractions yielded crystalline products on treatment with an alcoholic solution of mercuric chloride. Analyses of the mercury precipitates indicated the presence of ethyl, propyl and butyl sulphides. No thiophenes or mercaptans were detected. Charitschkoff[130] also showed the presence of thioethers in Grosny naphtha by means of mercuric chloride. By diluting the sludge obtained in the refining of Persian petroleum, removing the separated oil and then extracting the aqueous layer with chloroform, Thierry[131] obtained an oil containing a large number of sulphur compounds. From the low-boiling fractions he was able to isolate methyl ethyl sulphide, and another compound which was either methyl propyl or methyl isopropyl sulphide.

CHEMICAL PROPERTIES OF THE THIOETHERS

The property of thioethers of forming addition compounds with mercuric chloride has served as a means of identifying some of the sulphur compounds in the sulphuric acid extract obtained in refining various crude petroleum oils. Other metallic halides, such as mercuric iodide, titanium tetrachloride and platinic chloride, react similarly. The thioethers, however, form addition compounds with other substances. For example, ethyl sulphide when heated at 150° C. in a sealed tube with sulphur yields a mixture of the di-, tri-, tetra-, and (possibly) penta-sulphides.[132] Bromine also forms addition products, such as $(C_2H_5)_2SBr_2$, which may be converted to the corresponding iodine derivatives by treatment with potassium iodide.[133]

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[127] Wiezevich, Turner and Frolich, *Ind. Eng. Chem.*, 1933, **25**, 295.

[128] For bibliography of the sulphur compounds occurring in petroleum, shale and tar oils, see Borgstrom and Reid, *Oil and Gas J.*, 1927, **26**, 352.

[129] *Ber.*, 1889, **22**, 3303; *Chem. Soc. Abs.*, 1890, **58**, 350.

[130] *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 655; *Chem. Soc. Abs.*, 1900, **78** (2), 147; see Engler-Höfer, "Das Erdöl," Verlag von S. Hirzel, Leipzig, 1913, **1**, 477.

[131] *J.C.S.*, 1925, **127**, 2756.

[132] Böttger, *Ann.*, 1884, **223**, 349.

[133] Rathke, *Ann.*, 1869, **152**, 214.

This reaction with bromine has served as the basis for the estimation of thioethers in benzene, or other hydrocarbon solvent which is free of unsaturated hydrocarbons.[134] The solution of thioether is treated with bromine water, the excess bromine removed by the addition of potassium iodide, and iodine liberated is reduced with sodium thiosulphate. Hydrogen bromide is then extracted from the benzene solution with water and titrated with a dilute (0.05*N*) alkaline solution. The hydrogen bromide is formed as a result of the hydrolysis of the bromine addition product.[135] The reactions involving the formation of this addition product and its hydrolysis are:

$$R_2S + Br_2 \longrightarrow R_2SBr_2$$
$$R_2SBr_2 + H_2O \longrightarrow R_2SO + 2HBr$$

An interesting class of compounds, however, are those designated sulphonium (to show the analogy to ammonium compounds) and prepared by the interaction of the thioethers with alkyl iodides. To illustrate, methyl diethyl sulphonium iodide is formed when a mixture of ethyl sulphide and methyl iodide is allowed to stand for 2 to 3 days,[136] thus:

$$(C_2H_5)_2S + CH_3I \longrightarrow CH_3(C_2H_5)_2SI$$

The sulphonium compounds react with silver oxide and water to yield corresponding sulphonium hydroxides, which are strong bases and from which various salts may be prepared:

$$(C_2H_5)_3SI + AgOH \longrightarrow AgI + (C_2H_5)_3S.OH$$

Mild oxidizing agents, such as nitric acid of specific gravity 1.2, convert the thioethers to sulphoxides, and with more vigorous oxidizing agents the sulphone is obtained.[137] It is also possible to oxidize the sulphoxide to the sulphone, thus:

$$2(C_2H_5)_2S + O_2 \longrightarrow 2(C_2H_5)_2SO \text{ (sulphoxide)}$$
$$(C_2H_5)_2S + O_2 \longrightarrow (C_2H_5)_2SO_2 \text{ (sulphone)}$$

The sulphoxide is easily reduced with zinc and sulphuric acid to the thioether. Ethyl sulphoxide has been suggested as a plasticizer for pyroxylin.[138]

Two general methods of synthesizing thioethers are: the interaction of (1) alkyl halides and potassium (or sodium) sulphide, and (2) alkyl halides and potassium (or sodium) mercaptides. The latter method is analogous to that employed to make ethers, and permits the preparation of mixed thioethers (that is, thioethers containing two different alkyl radicals):

$$(1)\quad 2C_2H_5Cl + K_2S \longrightarrow 2KCl + (C_2H_5)_2S$$
$$(2)\quad CH_3I + C_2H_5SNa \longrightarrow NaI + CH_3SC_2H_5$$

Sabatier and Mailhe[139] reported that the passage of ethyl mercaptan over a cadmium sulphide catalyst at 320° to 330° C. resulted in the formation of ethyl sulphide and hydrogen sulphide. At a higher temperature (380° C.) ethylene and hydrogen sulphide were the main products. Wiezevich, Turner and Frolich[140] found that 45 to 55 per cent yields of thioethers were obtained from mercaptans at 350° C. when using a catalyst consisting of cadmium sulphide, zinc sulphide, and aluminum oxide.

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[134] Sampey, Slagle and Reid, *J.A.C.S.*, 1932, 54, 3401.

[135] Patein, *Bull. soc. chim.*, 1888, (2) 50, 203; *Chem. Soc. Abs.*, 1889, 56, 234.

[136] Klinger and Maasen, *Ann.*, 1888, 243, 199.

[137] Saizew, *Ann.*, 1867, 144, 154. Bechmann, *J. prakt. Chem.*, 1878, (2) 17, 452. For the preparation of disulphones, see Stutz and Shriner, *J.A.C.S.*, 1933, 55, 1242; and Gibson, *J.A.C.S.*, 1933, 55, 2611.

[138] Wiezevich, Turner and Frolich, *loc. cit.*

[139] *Compt. rend.*, 1910, 150, 1569.

The thioethers, particularly those derived from low molecular weight paraffins, are liquids possessing boiling points lying between those of the corresponding mercaptans and disulphides. See Table 95.

TABLE 95.—*Boiling Points of Sulphur Compounds.*

	Mercaptan ° C.	Thioether ° C.	Disulphide ° C.
Methyl	5.8	37.5–38	116–118
Ethyl	37	92–93	153–153.5
n-Propyl	67–68	141.5–142.5	192.5
n-Butyl	97–98	182	—

A possible application of thioethers is as solvents for various materials. Wiezevich, Turner and Frolich[141] have pointed out that these compounds dissolve rubber, as well as resins such as abietic acid, paracumaron, petroleum resin, and m- and p-cresol-sulphur chloride resins, and that cellulose nitrate is soluble in mixtures of ethyl alcohol and ethyl sulphide or methyl alcohol and propyl sulphide.

THIOPHANES

The thiophanes were isolated by Mabery and Quayle[142] from fractions of a Canadian petroleum using an alcoholic solution of mercuric chloride. The lower members of the series formed crystalline precipitates while viscous or oily masses were obtained from the higher members. The thiophanes were obtained in the free state by treating the mercuric chloride derivatives with hydrogen sulphide. The general formula for this series is $C_nH_{2n}S$ and hence they correspond to hydrothiophenes, thiophene having the formula C_4H_4S. They were therefore called thiophanes.

The thiophanes isolated, and some of their physical properties, are given in Table 96.

TABLE 96.—*Physical Properties of Thiophanes Isolated from a Canadian Petroleum.*

		B.P. at 50 mm. ° C.	Sp. Gr. (20°)	n_D
Hexylthiophane	$C_6H_{12}S$	55–57	—	—
Heptylthiophane	$C_7H_{14}S$	74–76	0.8878	1.468
Octylthiophane	$C_8H_{16}S$	81–83	0.8929	1.4860
iso-Octylthiophane	$C_8H_{16}S$	94–96	0.8937	—
Nonylthiophane	$C_9H_{18}S$	106–108	0.8997	1.4746
Decylthiophane	$C_{10}H_{20}S$	114–116	0.9074	1.4766
Undecylthiophane	$C_{11}H_{22}S$	128–130	0.9147	1.480
Tetradecylthiophane	$C_{14}H_{28}S$	168–170	0.9208	1.4892
Hexadecylthiophane	$C_{16}H_{32}S$	184–186	0.9222	1.4903
Octadecylthiophane	$C_{18}H_{36}S$	198–202	0.9235	1.4977

These thiophanes are characterized by the ease with which they react. They are readily oxidized by potassium permanganate or by chromic acid to sulphones, all of which are thick heavy oils having high boiling points and specific gravities greater than that of water. They react with ethyl iodide to form addition compounds, $C_nH_{2n}S \cdot C_2H_5I$. These latter compounds when warmed with silver oxide and water are converted to the corresponding hydroxides which show an alkaline reaction. The thiophanes also react violently with bromine with the evolution of hydrogen bromide in quantities equivalent to the bromine added. The chloroplatinates of the thiophanes are heavy, viscous oils.

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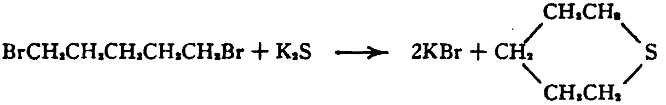
[140] *Ind. Eng. Chem.*, 1933, **25**, 295.

[141] *Loc. cit.*

[142] *Amer. Chem. J.*, 1906, **35**, 404; *Chem. Soc. Abs.*, 1906, **90** (1), 394.

Thierry[143] has isolated both tetramethylene sulphide and pentamethylene sulphide from the sludge obtained by treating Persian petroleum with sulphuric acid.

While tetrahydrothiophene and the other thiophanes were not well known at the time Mabery and Quayle reported their existence in petroleum distillates, some of them (tetrahydrothiophene and pentamethylene sulphide) were later synthesized by von Braun and Trümpler.[144] Their method was to allow potassium sulphide to react with the dibromide of the corresponding hydrocarbon. Pentamethylene sulphide, for example, was made from 1,5-dibromopentane and potassium sulphide, thus:



These thiophanes are liquids possessing very disagreeable odors. Tetrahydrothiophene boils at 119° C., and pentamethylene sulphide at 141° C.

In a similar manner Grischkevich-Trokhimovski[145] has prepared thiophanes containing three, four, five and six carbon atoms in the nucleus. These thiophanes exhibit the general properties of organic sulphides, i.e., they form sulphones, sulphonium compounds, dibromides (which are unstable), and addition products with mercuric chloride.

The reactions of two thiophanes, tetramethylene and pentamethylene sulphides, were later investigated by Bost and Conn.[146] The solvents used in this work were n-heptane and three different naphthas. From both heptane and naphtha solutions these thiophanes yield crystalline precipitates with mercuric chloride; oxidizing agents such as nitric acid, potassium permanganate, and hydrogen peroxide convert them to sulphones; methyl iodide reacts with them to yield the corresponding addition products; and bromine and mercuric iodide form unstable products with the thiophanes. Comparing the reactions of the thiophanes with those of ethyl sulphide and thiophene, under the same conditions, the indications are that the thiophanes more closely resemble alkyl sulphides than thiophene.

The behavior of trimethylene sulphide in heptane and naphtha solutions was studied also.[146a] This thiophane gave stable derivatives with mercuric chloride and methyl iodide. Sulphones were obtained on treatment with potassium permanganate or 30 per cent hydrogen peroxide. With bromine it yielded an orange-yellow precipitate, which was unstable, decomposing even at —15° C. Highly polymerized compounds resulted from the action of nitric or hydrochloric acid on trimethylene sulphide, which distinguishes it from tetra- and penta-methylene sulphides. Like these higher members, however, it resembles alkyl sulphides in chemical properties more than thiophene.

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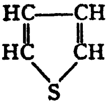
[143] *J.C.S.*, 1925, **127**, 2756.
[144] *Ber.*, 1910, **43**, 545.
[145] *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880, 901, 928, 944; *Chem. Abs.*, 1917, 11, 784, 785, 786.
[146] *Ind. Eng. Chem.*, 1931, **23**, 93; *Brit. Chem. Abs.* **A**, 1931, 464.
[146a] Bost and Conn, *Ind. Eng. Chem.*, 1933, **25**, 526.

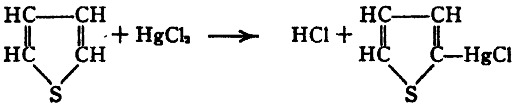
OTHER SULPHUR COMPOUNDS

The presence of thiophene in petroleum oils has been reported by a number of workers. Edeleanu and Filiti[147] found that certain Rumanian crude oils gave the characteristic thiophene reaction with isatin and sulphuric acid, and Meyer and Nahnsen[148] showed the presence of this same compound in the naphtha from some German crude oils.

In its chemical properties thiophene,



resembles benzene more closely than it does the aliphatic thioethers. For example, halogens react with it to yield substitution products rather than to saturate the double bonds or to add halogen to the sulphur. Formulas of representative compounds of this type are C_4H_3BrS and $C_4H_2Cl_2S$. Nitric acid and sulphuric acid react with thiophene to yield nitro-compounds and sulphonic acids, respectively. The reaction with mercuric chloride differs from the corresponding reaction of aliphatic thioethers and mercuric salts in that one chlorine atom is eliminated as hydrogen chloride and the mercury becomes attached to the thiophene nucleus, thus:



According to McKittrick,[149] the HgCl radical enters the *a* or 2 position if that is unoccupied, otherwise the *β* or 3 position; the latter reaction is much slower than the former. Both types of derivatives are soluble in alcohol and other organic solvents. If both *a* positions are unoccupied, then a mixture of the *a*-mono- and *a,a′*-dimercuric chloride derivatives is formed. These dimercuric chloride compounds are extremely insoluble in all common organic solvents.

SULPHUR COMPOUNDS IN CRACKED DISTILLATES

The types of organic sulphur compounds thus far mentioned have been those occurring in crude petroleum oil or its distillates. Some of the same types, however, have been found in the cracked distillates from petroleum oils. For example, Tomekichi Kan,[150] using a cracked distillate having a density of 0.834, an iodine number of 48.02, and a sulphur content of 1.15 per cent, found that on agitating this oil with an alcoholic solution of mercuric chloride the compounds, $C_2H_6SHgCl_2$ and $C_4H_{10}SHgCl_2$, were precipitated. Along with these substances similar compounds of their higher homologues and also polymerization products were obtained. Dudenko[150a] reported a pressure distillate (boiling range, 40° to 231° C.) containing 0.005 per cent elemental sulphur, 0.01 per cent sulphur as hydrogen sulphide, 0.004 per cent as mercaptans, 0.006 per cent as disulphides, 0.003 per cent as thioethers and 0.038 per cent as other sulphur compounds.

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[147] *Bull. soc. chim.*, 1900, **23** (3), 382; *Chem. Soc. Abs.*, 1900, **78** (2), 486. See also Engler-Höfer, "Das Erdöl," Verlag von S. Hirzel, Leipzig, 1913, 1, 472.

[148] *Ber.*, 1885, **18**, 217.

[149] *Ind. Eng. Chem.*, 1929, **21**, 585.

[150] *J. Soc. Chem. Ind. (Japan)*, 1927, **30**, 129.

[150a] *Azerb. Neft. Khoz.*, 1931, No. 6, 42; *Chem. Abs.*, 1932, **26**, 289.

Some information about the sulphur compounds occurring in a naphtha obtained by cracking the fuel oil from Midway (California) crude petroleum has been given by McKittrick.[149] The sample of naphtha was subjected to a series of fractional extractions using, first, liquid sulphur dioxide at —20° to —30° C.; second, aniline at —10° to —20° C.; and finally ethylene glycol diacetate also at —10° to —20° C. From 212 liters of the original naphtha, having a specific gravity of 0.786 at 15° C. and a sulphur content of 1 per cent, 13.6 liters of oil extract, having a specific gravity of 0.900 at 15° C. and 5.5 per cent sulphur, were obtained. This extract represented 40 per cent of the total sulphur in the original distillate; of the rest, 25 per cent remained in the residual oil from the liquid sulphur dioxide treatment and 35 per cent in the various low sulphur fractions obtained on extraction with aniline or with ethylene glycol diacetate and which were discarded. The oil extract was distilled up to 160° C. at atmospheric pressure and then the distillation completed at 120 mm. pressure, taking cuts every 2.5° C.

The sulphur compounds identified in these fractions were thiophene and its homologues. These were precipitated as the mercuric chloride derivatives by dissolving the different fractions in small quantities of alcohol and adding an aqueous solution of mercuric chloride, together with sodium acetate. The mercury derivatives were separated by their solubility in hot alcohol, and the sulphur compound liberated by decomposing these derivatives with 6*N* hydrochloric acid. The sulphur compounds thus isolated and identified were: thiophene, 2-methyl- and 3-methylthiophene, 2,3-dimethylthiophene, 3,4-dimethylthiophene, 2-ethyl- and 3-ethylthiophene. All of these compounds were found in the fractions boiling below 160° C. at atmospheric pressure.

McKittrick also attempted to isolate some of the sulphur compounds which were present in the sludge obtained by the low temperature acid treating of cracked naphtha. He isolated two compounds which appeared to contain eight and eleven carbon atoms, respectively, although their structures were not determined. Their chemical properties, however, were very similar to those of compounds isolated by Mabery and Quayle[142] from the sludge formed in treating Canadian kerosene.

USES OF SULPHUR COMPOUNDS FROM PETROLEUM

One use for the mineral oil products possessing a high sulphur content is as a denaturant for ethyl alcohol, under the trade name *Alcotate,* to replace methyl alcohol.[151] The specifications for this product are as follows: Specific gravity at 15.5° C. must not be less than 0.850. Sulphur content must be not less than 4.5 per cent. No added hydrogen sulphide, carbon disulphide or elementary sulphur is to be present. Upon distillation 20 per cent must distil over at 175° C., 50 per cent at 195° C., and 90 per cent at 245° C. Alcotate must mix with an equal volume of 95 per cent alcohol and show no separation. The addition of 8 cc. of water to 25 cc. of a 1.5 per cent solution of Alcotate in 95 per cent alcohol should produce no more turbidity than that shown by the addition of 1.5 grams of chemically pure lead acetate to 25 cc. of water.

Highly refined petroleum oils have been used as insecticides for certain insects on nearly every type of orchard crop. The oil emulsions used generally have an oil concentration of about 60 to 90 per cent and before application are diluted with water to the range from 0.75 to 5.0 per cent. Oils containing a high percentage of organic sulphur possess a high fungicidal as well as insecticidal value.[152]

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[151] *Petroleum Z.*, March 18, 1931, *Motorenbetreib und Maschinen-Schmierung,* 15. *Cf. Ind. Eng. Chem.*, 1931, 23, 2.

A product called *Cal-Odorant No. 3,* developed by the Standard Oil Co. of California, is a mixture of hydrocarbons and sulphur compounds and is marketed for odorizing natural gas.[153] About 3 gallons of this odorant per million cubic feet of gas are required. This application of sulphur compounds is similar to the use of mercaptans in manufactured gas. Organic sulphur compounds, which are intended as odorants for the detection of gas leakage, can be prepared either by sulphonating hydrocarbons with sulphuric acid at 100° C. followed by cracking, or by cracking the waste acid obtained in the refining of cracked distillates.[154]

The addition of a small proportion of carbon bisulphide, ethyl mercaptan or ethyl sulphide to a non-cutting oil in an oil well or pipe line to prevent accumulation of solid matter has been proposed.[155] (By non-cutting oil is meant an oil which does not possess emulsifying powers.) These sulphides act as emulsifying agents and assist solid materials to be carried along by the oil stream rather than permitting them to deposit on the walls of the casing or in other places.

Mixtures of sulphur compounds, such as n-propyl disulphide, methyl disulphide, benzyl sulphide or disulphide, carbon disulphide or thiocarbonates, with vegetable protein material have been proposed as adhesives.[155a] The stabilization of chlorinated hydrocarbons, e.g., carbon tetrachloride, trichloroethylene or tetrachloroethylene, with a small proportion of butyl mercaptan is suggested by Stewart and DePree.[155b]

THERMAL DECOMPOSITION OF SULPHUR COMPOUNDS

Some information regarding the thermal decomposition in the vapor phase of sulphur compounds of the types representative of those present in petroleum has been given by Faragher, Morrell and Comay.[156] These workers investigated the decomposition of pure compounds both alone and dissolved in petroleum oils. Most of their investigations wese carried out at 496° C. (925° F.), which is within the temperature range used industrially for the cracking of petroleum oils.

The pure compounds, or their solutions in naphtha, were allowed to flow directly into a reaction tube, where they were flashed into a vapor. The average temperature of the tube was 496° C. The products of decomposition were passed through a condenser, and both the liquid condensate and the uncondensed gases analyzed.

Disulphides, such as the ethyl, n-propyl, and isoamyl, yielded hydrogen sulphide, mercaptans, thioethers and thiophene or its derivatives, together with some saturated and unsaturated gaseous hydrocarbons. From ethyl sulphide only hydrogen sulphide, mercaptans and the hydrocarbon gases were obtained, while isoamyl sulphide yielded the same products together with some thiophene derivatives and a small quantity of hydrogen (about 0.5 per cent) in the gases. Isoamyl mercaptan yielded elemental sulphur, a large quantity of hydrogen sulphide, a tarry residue, and hydrocarbon gases, no sulphides or thiophene derivatives being detected.

Isoamyl disulphide, n-propyl sulphide, and isoamyl sulphide were dissolved

[152] DeOng, *Ind. Eng. Chem.*, 1930, **22**, 836; *Chem. Abs.*, 1930, **24**, 4888.

[153] Holtz, *Gas-Age Record,* 1930, **66**, 341; *Chem. Abs.*, 1930, **24**, 5977.

[154] Piotrowski and Winkler, *Gas i Woda,* 1931, **11**, 307; *Chem. Abs.*, 1932, **26**, 2575.

[155] De Groote, U. S. Patent 1,844,883, Feb. 9, 1932; assigned to Tretolite Co.; *Chem. Abs.*, 1932, **26**, 2047.

[155a] Laucks, Inc., German Patent 532,325, 1927; *Chem. Abs.*, 1932, **26**, 267; British Patent 298,511, 1927; *Chem. Abs.*, 1929, **23**, 3061.

[155b] U. S. Patent 1,917,073, July 4, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 4539.

[156] *Ind. Eng. Chem.*, 1928, **20**, 527.

in a naphtha, obtained from Pennsylvania crude petroleum, and the vapors of these solutions passed through the reaction tube at 496° C. The main products of the reaction appeared to be elemental sulphur, hydrogen sulphide, and mercaptans. Substitution of elemental sulphur for the sulphur compounds yielded hydrogen sulphide as the only reaction product. The heat treatment of a naphtha solution of thiophene, at either 496° C. or 871° C. failed to show any thermal decomposition of this substance, though there was some loss of naphtha due to cracking at the latter temperature.

The thermal decomposition of aliphatic mercaptans dissolved in various solvents was investigated by Malisoff and Marks.[157] The solvents used were benzene, a mixture of n-heptane with 2,2,4-trimethylpentane, and a stable straight-run gasoline (end point about 150° C.) which was practically free of sulphur. The mercaptans used were n-propyl, n- and iso-butyl, n- and iso-amyl, and benzyl mercaptan. The temperatures varied over a range from about 300° to 475° C. The percentage decomposition increased with increasing temperatures, and also with increased time of passage of the gases through the heated zone. Branched-chain mercaptans were less stable than the corresponding straight-chain isomers, though only markedly so at the higher temperatures (particularly around 475° C.). Benzyl mercaptan was less stable than any of the lower aliphatic mercaptans. The solvent also appeared to exert some influence as benzene, compared to the straight-run naphtha, promoted decomposition, particularly of n-amyl mercaptan. The decomposition of this latter mercaptan was depressed by the addition of carbon dioxide or hydrogen. All the mercaptans on decomposition yielded hydrogen sulphide and an olefin.

Butyl sulphide dissolved in benzene (0.025 to °.3 molar solutions) was subjected to temperatures of 400° to 515° C. by Malisoff and Marks,[157a] the period of heating varying from 5 to 55 seconds. The products of the reaction were hydrogen sulphide and mercaptans. No decomposition occurred at 400° C., moderate decomposition at 500° C., and at 515° C. with 30 seconds exposure only 20 per cent conversion of the sulphide was obtained. In the presence of a large proportion of hydrogen sulphide, thiophene and free sulphur were formed in addition to the products mentioned. The reaction is not unimolecular and is catalyzed by glass surfaces or by aluminum oxide. Comparison of the rates of decomposition in benzene and in n-heptane solutions indicated benzene probably accelerated the reaction and that n-heptane may be an inhibitor. Butyl sulphide appeared to be more stable than the corresponding mercaptan.

Trenner and Taylor[157b] reported that the thermal decomposition of ethyl mercaptan or sulphide, at 380° to 410° C. under 50 to 440 mm. pressure, yielded hydrogen sulphide, ethylene and polysulphides. An intermediate product, boiling at 48° to 49.5° C. and possibly a dimercaptan ($C_2H_5SH{=}SHC_2H_5$), was isolated in both instances.

In studying the cracking of a high sulphur (3.6 per cent) gas oil, particularly with reference to the formation of carbon disulphide, Holtz[158] observed that no carbon disulphide was obtained at 649° C., a small quantity at 732° C., and at 982° C. a large quantity of this material was formed. When a sulphur-free oil was cracked at about 850° C. in the presence of a gas containing hydrogen sulphide, no carbon disulphide was formed unless the hydrogen sulphide was present in large proportions. Even in the absence of carbon disulphide formation, a large disappearance of hydrogen sulphide during the cracking operation was noted. Furthermore, on passing hydrogen sulphide over sugar charcoal at 850° C., neither hydrogen sulphide nor carbon disulphide could be discovered at first in the exit gas; after a time, a gradually increasing quantity of hydrogen sulphide could be detected; and finally, after a still further time interval carbon disulphide was found among the reaction products. The charcoal at the end of the experiment contained 2.8 per cent sulphur.

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[157] *Ind. Eng. Chem.*, 1931, **23**, 1114; *Brit. Chem. Abs.* **A**, 1931, 1393.

[157a] *Ind. Eng. Chem.*, 1933, **25**, 780.

[157b] *J. Chem. Phys.*, 1933, **1**, 77; *Chem. Abs.*, 1933, **27**, 1809.

[158] *Fuel*, 1931, 10, 16; *Brit. Chem. Abs.* **B**, 1931, 428. See also Holtz and Huff, *Ind. Eng. Chem.*, 1927, **19**, 1268; and *Proc. Am. Gas Assoc.*, 1927, 1431; *Chem. Abs.*, 1928, **22**, 4770.

These phenomena are attributed to the formation of a solid carbon-sulphur complex. It is suggested that the surfaces of carbon when exposed at the temperatures used in gas-making to gases containing sulphur, first absorb sulphur from these gases, which aids in the further decomposition of sulphur compounds. The ability to absorb sulphur gradually decreases and a degree of saturation is approached before carbon disulphide is evolved. Although sulphur appears to resemble oxygen in forming a complex with carbon no exact analogue of carbon monoxide was isolated.

Rosen and Lieber [158a] described a process for the conversion of organic sulphur compounds to hydrogen sulphide by passing the gases over a catalyst consisting of ferrous sulphide and a promoter, the latter being an oxide or sulphide of the metals of Groups III or VI of the Periodic System. The temperatures employed varied from 337° to 482° C.

EFFECT OF REFINING AGENTS ON SULPHUR COMPOUNDS

The literature dealing with the refining of petroleum distillates, particularly those distillates containing a high percentage of sulphur compounds, is voluminous. No attempt is made here to review such a vast field exhaustively, but rather to indicate some of the fundamental physical and chemical properties of the sulphur compounds which are the bases for such methods.

Solvent extraction [159] of sulphur compounds is the most common procedure for their removal, and sulphuric acid is apparently the best solvent.[160] In addition to its action as a solvent this acid also exerts other effects, for example, its oxidizing action on mercaptans. The disadvantages connected with its use, particularly with cracked distillates, are that it either polymerizes the unsaturated hydrocarbons or reacts with them to form alkylsulphuric acids. Refining at low temperatures, 3° C. or lower, has been suggested as a means of overcoming these latter two effects.[161] Gary [161a] recommended sulphur trioxide dissolved in liquid carbon dioxide.

Petroleum oils, possessing a high-sulphur content, are reported to be substantially desulphurized by liquid ammonia.[161b] The oil is mixed with liquid anhydrous ammonia (under pressure) in the presence of catalysts, e.g., metallic sodium, potassium, calcium or barium. Some of the ammonia is converted to ammonium sulphide, or complex ammonium sulphur compounds, which may be recovered from the oil by extraction with water or by heating the oil with ammonia vapor and steam. Oxidation of the ammonium compounds yields ammonium sulphate. The latter may be obtained directly by treating the oil with liquid ammonia and ozone or ammonium persulphate.

[158a] British Patent 391,660, 1933; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 4910. Also French Patent 741,372, 1932; *Chem. Abs.*, 1933, 27, 2742.

[159] Wood, Lowy and Faragher, *Ind. Eng. Chem.*, 1924, 16, 1116. Wood, Sheely and Trusty, *Ind. Eng. Chem.*, 1926, 18, 169. Youtz and Perkins, *Ind. Eng. Chem.*, 1927, 19, 1247.

[160] Woodward (*Ind. Eng. Chem.*, 1929, 21, 1233) records an investigation in which sixty-one different organic solvents were employed for this purpose. None of these, however, are apparently equal to sulphuric acid as an extracting agent.

[161] Davis, Hampton and Klemgard, U. S. Patent 1,705,809, March 19, 1929; *Chem. Abs.*, 1929, 23, 2290. See also Davis and Hampton, U. S. Patent 1,869,885, Aug. 2, 1932; assigned to Standard Oil Co. of California; *Chem. Abs.*, 1932, 26, 5413.

[161a] U. S. Patent 1,893,138, Jan. 3, 1933; *Chem. Abs.*, 1933, 27, 2291.

[161b] Clancy, U. S. Patents 1,423,710, 1,423,711 and 1,423,712, July 25, 1922; *Chem. Abs.*, 1922, 16, 3202; Canadian Patents 215,380, 215,386 and 215,387, 1922; *Chem. Abs.*, 1922, 16, 1148.

A large number of solid adsorption agents have been proposed for the removal of sulphur compounds.[162] Included among these are: fuller's earth, silica gel,[163] aluminum oxide, aluminum chloride, and mercuric chloride or acetate. Holmes[164] reported that metallic sulphides disseminated throughout "red gels" (made by mixing dilute solutions of ferric chloride and sodium silicate) are good adsorbents for sulphur compounds of the thiophene type. Of the sulphides investigated, cupric sulphide appeared to be the best.

Oxidizing agents have been suggested as reagents for removing sulphur compounds. The reactions probably involved are the oxidation of thioethers to sulphones, which are soluble and can be removed by washing with water, and of other sulphur compounds, such as mercaptans, to sulphonic acids, removed by washing with an alkaline solution. Thus, using pentamethylene sulphide as an example of the thiophanes, Borgstrom, Bost and McIntire[165] have shown that when dissolved in naphtha it is almost completely removed by refluxing with permanganate solution, or by washing with sodium hypochlorite solution. Other oxidizing agents which have been proposed are oxygen, ozone, or ozonized oxygen.[166]

Wood, Lowy and Faragher[167] observed that solutions of sodium hypochlorite convert mercaptans to disulphides, but have little effect on other types of sulphur compounds. Birch and Norris,[167a] however, reported that alkyl sulphides are converted to sulphones by sodium hypochlorite solutions, and as the sulphones are soluble in water (solubility, of course, varies with the molecular weight) this permits extraction of sulphur compounds. Wood, Greene and Provine[168] also observed the desulphurizing effect of hypochlorite solutions on naphtha containing various sulphur compounds. This effect was dependent on the type and molecular weight of the sulphur compound, the degree of alkalinity of the hypochlorite solutions, the quantity of available chlorine, and the time and intensity of agitation of the hypochlorite solution and naphtha. All investigators are agreed that thiophene is not removed by hypochlorite solutions.

In the Frasch[169] process, high sulphur oils are heated with copper oxide, or a mixture of copper and lead oxides. Probably the sulphur compounds are not only oxidized by these metallic oxides with the formation of the corresponding metallic sulphides, but in addition the mercaptans react with these oxides to yield mercaptides, which decompose on heating to thioethers and metallic sulphides. The reactions with lead oxide, for example, may be represented as:

$$\mathrm{PbO + 2RSH \longrightarrow Pb(SR)_2 + H_2O}$$
$$\mathrm{Pb(SR)_2 \longrightarrow R_2S + PbS}$$

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[162] Wood, Sheely and Trusty, *loc. cit.* Youtz and Perkins, *loc. cit.* Borgstrom and McIntire, *Ind. Eng. Chem.*, 1931, **23**, 321. The use of metallic chlorides was described by Halloran, Chappell and Osmer, U. S. Patent 1,872,446, Aug. 16, 1932; assigned to Standard Oil Co. of California; *Brit. Chem. Abs.* **B**, 1933, 615.

[163] Tschufarow and Litovtschenko (*J. Chem. Ind., Moscow,* 1931, **8**, 65; *Brit. Chem. Abs.* **B**, 1931, 524) have reported that this substance removes only mercaptans. More effective sulphur removal is secured by a combination of treating with sulphuric acid and with silica gel.

[164] U. S. Patent 1,882,146, Oct. 11, 1932; *Chem. Abs.*, 1933, **27**, 593. See also Holmes, Elder and Beeman, *J. Phys. Chem.*, 1932, **26**, 2981; *Chem. Abs.*, 1933, **27**, 1491.

[165] *Ind. Eng. Chem.*, 1930, **22**, 87.

[166] Bruzac, British Patent 346,152, 1929; assigned to M. Mercurio; *Chem. Abs.*, 1932, **26**, 589. For desulphurization of brown-coal tar distillates with ozone, see Maneck, *Braunkohlenarch.*, 1933, No. 40, 53; *Chem. Abs.*, 1933, **27**, 4907.

[167] *Loc. cit.*

[167a] *J.C.S.*, 1925, **125**, 1934.

[168] *Ind. Eng. Chem.*, 1926, **18**, 823.

[169] U. S. Patents 543,619, July 30, 1895, and 622,799, April 11, 1899. Additional suggestions of Frasch are reviewed in Kalichevsky and Stagner, "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933, 264, and in Engler-Höfer, "Das Erdöl," Verlag von S. Hirzel, Leipzig, 1913, **3**, 546.

With some petroleums, a mixture of 70 per cent copper oxide, 15 per cent lead oxide, and 15 per cent iron oxide yields better results.[170] Also, passing the vapors of the petroleum distillate, together with steam, over iron ore effects a reduction of sulphur of over 80 per cent, accompanied by the evolution of large quantities of hydrogen sulphide. At the same time considerable cracking of the distillate takes place, and the pores of the contact mass become filled with carbon which can be only partially removed by steam. The use of a mixture of iron and copper oxides (obtained on burning pyrites of iron and copper) in a similar manner is described by Blagodorov.[171] Cross[172] has suggested desulphurizing and degumming the hydrocarbons produced by cracking by passing them, either in the liquid or vapor phase, first through a bed of a metal (or its oxide) and then through a bed of adsorbent clay, such as bentonite.

Kogerman[173] reported that metals, such as nickel or copper, are not satisfactory for the vapor-phase desulphurization of Esthonian shale-oil distillates. An effective procedure is the hydrogenation of such distillates at temperatures of 300° to 400° C., and at pressures of 900 to 1000 atmospheres. Guthke[173a] removed sulphur compounds from hydrocarbons by treatment with hydrogen at 100° to 300° C. in the presence of a metallic sulphide (nickel or molybdenum sulphide) and an activator, e.g., cobalt or chromium oxide. The applied pressure was less than that required for hydrogenation of the hydrocarbons. Pease, Keighton and Munro[173b] partially eliminated thiophene from benzene by hydrogenation at atmospheric pressure in the presence of mixed catalysts consisting of cobalt or chromium oxide or sulphide and molybdenum oxide or sulphide.

A method suggested for the elimination of sulphur compounds from industrial gases is scrubbing with an alcoholic solution of sodium hydroxide. In another procedure mixtures of hydrocarbon gases, or vapors, are desulphurized[174] by conducting them over a thorium or thorium oxide catalyst at a temperature of about 650° C. Promoters can be used, such as magnesium oxide, lead oxide, copper or nickel. In such a process the sulphur-containing substances are converted to hydrogen sulphide, which is then removed from the gaseous mixture. The catalytic mass is regenerated by air, steam or hydrogen.[175]

Lachman[176] has described a vapor-phase process for the removal of sulphur compounds in which the vapors of gasoline, or other petroleum distillates, are passed countercurrent to a concentrated solution of a metallic salt at temperatures ranging from 200° to 260° C. An example of such a reagent is an 80 per cent solution of zinc chloride to which 0.5 to 3.0 per cent zinc hydroxide has been added. To prevent evaporation or concentration of the solution steam or water may be added to the hydrocarbon vapors. Salts of other metals, such as those of cadmium, mercury, iron, cobalt, nickel, chromium, copper, manganese and aluminum, may be employed. Kubulnek[177] has reported that this method of treatment removes sulphur compounds which are rendered inactive by the doctor treatment, but which are reactivated under conditions existing in an internal-combustion engine and cause corrosion. He also pointed out the advisability of washing the petroleum distillate with 5 per cent sodium hydroxide solution before subjecting it to the Lachman process. Heating petroleum oils, under pressure, in the presence of metallic chlorides, particularly titanium chloride, is said to convert the stable sulphur compounds into sulphur derivatives which may be eliminated with sodium plumbite solution.[177a] Pretreatment with ferric chloride, to remove oxygenated compounds, was recommended.

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[170] Postovsky and Plyusnin, *Neft. Khoz.*, 1930, **19**, 561; *Brit. Chem. Abs.* **B**, 1931, 1034.

[171] Russian Patent 27,431, 1931; *Chem. Abs.*, 1933, **27**, 2291.

[172] U. S. Patent 1,840,158, Jan. 5, 1932; assigned to Cross Development Corp.; *Brit. Chem. Abs.* **B**, 1932, 971. *Cf.* Gary, Canadian Patent 328,684, 1932; assigned to Minerals Increment Co.; *Chem. Abs.*, 1933, **27**, 1154.

[173] *J. Inst. Fuel*, 1932, **5**, 278; *Chem. Abs.*, 1932, **26**, 5740.

[173a] U. S. Patent 1,897,798, Feb. 14, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2691.

[173b] *Ind. Eng. Chem.*, 1933, **25**, 1012.

[174] For a discussion of desulphurizing petroleum distillates by hydrogenation see Ellis, "Hydrogenation of Organic Substances." D. Van Nostrand Co., New York, 1930.

[175] Al and Moser, U. S. Patent 1,819,055, Aug. 18, 1931; *Chem. Abs.*, 1931, **25**, 5753; and German Patent 535,848, 1929; *Chem. Abs.*, 1932, **26**, 1046. Both patents assigned to Bataafsche Petroleum Maatschappij. Also Dutch Patent 22,257, 1930; *Chem. Abs.*, 1930, **24**, 5087.

[176] U. S. Patents 1,790,622, Jan. 27, 1931; 1,809,170, June 9, 1931; 1,826,138, 1,826,139, 1,826,140, 1,826,141, 1,826,142, 1,826,143, 1,826,144, 1,826,145, 1,826,146, 1,826,147, Oct. 6, 1931; all assigned to Richfield Oil Co. of California; *Chem. Abs.*, 1932, **26**, 589. Also Richfield Oil Co. of California, British Patent 353,055, 1930; *Brit. Chem. Abs.* **B**, 1931, 915.

[177] *Neft. Khoz.*, 1932, **22**, 104, 175; *Brit. Chem. Abs.* **B**, 1932, 968, 969.

Vaporizing petroleum hydrocarbons and subjecting them to the action of ultraviolet light in the absence of oxidizing gases but in the presence of a porous contact mass in which sulphur-containing condensation products are precipitated, is another proposed method.[177b] Egloff[177c] recommended the desulphurization of cracked hydrocarbon vapors with ozone in the presence of a silent electric discharge.

REACTIONS OF SULPHUR COMPOUNDS WITH METALS

Reactions with metals have been studied by Elgin, Wilder and Taylor[178] as a means for the removal of sulphur compounds from both straight-run and cracked naphthas. Two metals were employed, a reduced nickel oxide supported on kieselguhr, and a reduced iron catalyst containing potassium and aluminum oxides as promoters, which had been used for the synthesis of ammonia. Adsorption of sulphur compounds in the liquid phase was accomplished by agitating the naphtha with different weights of nickel. The amount of sulphur removed was proportional to the quantity of contact agent up to about 45 grams of nickel per 100 cc. of naphtha. From this point on, increasing the proportion of nickel gave only slightly greater sulphur removal, and under none of the conditions studied was complete removal of sulphur possible. Filtration of the naphthas through a column packed with the nickel yielded no better results than were obtained by agitation. A higher percentage of sulphur compounds, as shown in Table 97, was removed from cracked naphtha than from straight-run naphtha.

TABLE 97.—*Maximum Sulphur Adsorbed by Nickel from Liquid.*

Naphtha	Sulphur Content Initial	Sulphur Content Final	Sulphur Adsorbed
	Per Cent	Per Cent	Per Cent
Straight Run No. 1	0.410	0.210	46.0
Straight Run No. 2	0.278	0.165	40.7
Cracked No. 3	0.357	0.157	56.0

Nickel appears to adsorb certain sulphur constituents selectively from the naphthas, the quantity adsorbed being different for naphthas from different sources. For example, the mercaptans were completely removed from the cracked naphtha used but not from the straight-run naphthas. Sulphur compounds other than mercaptans were adsorbed in all cases. The adsorption appears to be irreversible, as no sulphur was removed by extraction of the used contact mass with sulphur-free naphtha. Reduced iron was very much less effective than reduced nickel.

[177a] Compagnie des mines de Vicoigne Noeux et Drocourt, French Patent 40,543, 1930; *Chem. Abs.*, 1933, **27**, 1500; addition to French Patent 691,118, 1929; *Chem. Abs.*, 1931, **25**, 1068.

[177b] Magnus, German Patent 500,718, 1927; *Chem. Abs.*, 1930, **24**, 4928.

[177c] U. S. Patent 1,803,964, May 5, 1931; assigned to Universal Oil Products Co.; *Brit. Chem. Abs.* B, 1932, 92.

[178] *Ind. Eng. Chem.*, 1930, **22**, 1284.

For the vapor-phase removal of sulphur compounds the vapors of the different naphthas were passed over the metals at 300° C., and the sulphur content of the condensed vapor determined at regular intervals. Sulphur removal was pronounced at first, but diminished until a steady state was reached, in which the reduction of sulphur was constant. The volume of naphtha vapor treated by the adsorbent before this steady state was attained, the percentage reduction of sulphur during this state, and the kinds of sulphur compounds removed appeared to depend upon the particular naphtha treated. All mercaptans, however, seemed to be removed. Sulphur is eliminated from distillates by this vapor-phase treatment in the form of hydrogen sulphide.

Redistillation of the naphthas treated in this way over fresh samples of the metals resulted in only very slight reduction of sulphur content. A third treatment did not further reduce the sulphur content. When hydrogen was added to the naphtha vapors (1 volume of hydrogen to 3.7 of vapor), a greater reduction of sulphur content was obtained, although the characteristics of the catalyst remained the same. Reduced iron, which is very effective in the synthesis of ammonia, was much less so than nickel for vapor-phase removal of sulphur.

Elgin,[179] in studying the adsorption of pure compounds from naphtha solutions by reduced nickel oxide, observed that mercaptans were removed to a larger extent than either alkyl sulphides or thiophene.

In the vapor-phase treatment of such naphtha solutions, with a nickel adsorbent (such as that described by Elgin, Wilder and Taylor) which had reached the steady state, alkyl mercaptans and sulphides seem to undergo a reaction evolving hydrogen sulphide, and the mercaptans seem to be more readily removed than the sulphides. Thiophene was not affected unless hydrogen was added to the naphtha vapors. Using a sulphur-free catalyst, thiophene sulphur can be removed, but the catalyst rapidly loses its activity.

Another proposed method is to heat the petroleum distillate in contact with precipitated, reduced copper, and then to filter off the excess copper and copper sulphide.[180] Sulphur compounds are removed as sulphides by subjecting the distillates to the action of tin, aluminum, copper, magnesium or their lower oxides followed by treatment with sodium zincate.[180a]

SULPHUR COMPOUNDS IN SHALE OIL

In discussing the sulphur compounds found in petroleum and its distillates, it is of interest to include a brief reference to those present in shale and shale oil.

Harding and Thordarson[181] have studied the distribution of sulphur in American (Colorado) oil shale. As a line of demarkation between coal and shale has never been sharply drawn, they used the methods of analysis which were in principle those employed by Parr and Powell[182] in their analyses of coal, and found the particular shale studied to contain:

	Per Cent
Total sulphur	1.373
Sulphate sulphur	0.0865
Sulphide sulphur	0.6375
Organic sulphur	0.649

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[179] *Ind. Eng. Chem.*, 1930, **22**, 1290.

[180] Feld, British Patent 332,910, 1929; assigned to Stadtberger Hütte A.-G.; *Chem. Abs.*, 1931, **25**, 521. *Cf.* Dittrich, *Brennstoff-Chem.*, 1933, **14**, 283; *Brit. Chem. Abs.* **B**, 1933, 819.

[180a] Benzol-Verband G.m.b.H., German Patent 570,876, 1933; *Chem. Abs.*, 1933, **27**, 4388.

[181] *Ind. Eng. Chem.*, 1926, **18**, 731.

[182] *Univ. Illinois Exp. Sta. Bull.*, 1919, **111**.

After extracting the shale with phenol its sulphur content was 1.368 per cent, indicating only 0.005 per cent resinic sulphur, a negligible quantity. The humus sulphur content, the difference between organic and resinic sulphur, was 0.644 per cent. Practically all of the sulphide sulphur was present as pyrites, marcasite, or both.

The portion of Kimmeridge shale oil volatile with steam, amounting to about 30 per cent of the crude oil, was investigated by Challenger, Haslam and Bramhall.[183] This fraction was treated successively with hydrochloric acid (1:3), sodium hydroxide (10 per cent), and a saturated solution of sodium hydrogen sulphite. These removed amines, phenols and ketones, respectively. The purified product was then dried and distilled first at atmospheric pressure (to a temperature of 180° C.) and then under vacuum (27 mm. pressure). Various fractions obtained during the distillation were investigated to identify sulphur compounds present. Table 98 shows the boiling ranges of the various fractions and the sulphur compound isolated from each.

TABLE 98.—*Sulphur Compounds Isolated from Shale Oil Fractions.*

B.P., ° C.	Sulphur Compound Found
75–93	Thiophene
109–117	2-Methylthiophene
134–138	2-Ethylthiophene and 2,3-dimethylthiophene
158–167	A thiophene derivative, either propyl, methylethyl or trimethyl

Dodonov and Soshestvenska[184] have shown that thiophene, 2-thiotolene, and 2,3-thioxene occur in the 170° to 180° C. fraction from Russian shale oil. The isolation of such compounds must be preceded by a very careful and tedious fractionation of an appropriate portion of the oil.

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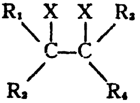
[183] *J. Inst. Pet. Tech.*, 1926, **12**, 106; *Chem. Abs.*, 1926, **20**, 3560. See also Challenger, *J.S.C.I.*, 1929, **48**, 622.

[184] *Ber.*, 1926, **59B**, 2202; *Chem. Abs.*, 1927, **21**, 490.

Chapter 20

Reactions of Olefins with Halogens. Olefin Dihalides and Their Derivatives

The olefin hydrocarbons as a class, and also all compounds possessing an olefinic linkage in their molecules, are characterized by their power of forming addition compounds with numerous chemical reagents. This characteristic distinguishes them from the paraffin hydrocarbons which are capable of forming substitution derivatives only, i.e., compounds in which one or more hydrogen atoms of the paraffin are replaced by other atoms or groups of atoms. The direct combination of the olefin hydrocarbons with halogens to yield, initially, dihalogen derivatives of the corresponding paraffin (or olefin dihalides), in which the two halogen atoms are attached to adjacent carbon atoms is an example of this power. The constitution of the olefin dihalides may be expressed in the general formula



where X is a halogen atom and R_1, R_2, R_3, and R_4 are hydrogen atoms or alkyl groups. It has been known for over a century that ethylene possessed this important property which has since been found to be a general reaction of the unsaturated hydrocarbons as a class. The reaction between monolefins and halogens is most vigorous in the case of bromine, chlorine comes second, and iodine reacts more slowly. It also appears to be a rule that the rate of halogenation of the simple monolefins increases with increasing molecular weight up to a maximum and then probably decreases, though constitutional influences play an important rôle.[1] In a few cases the combination of olefin with halogens is extremely slow because of steric hindrance. In actual practice, moreover, though the addition of halogens to olefins occurs rapidly, substitution also takes place to some extent with the production of polyhalogen compounds. This is especially true when the olefin contains reactive hydrogen atoms, readily replaceable.

The power of unsaturated hydrocarbons of directly combining with halogens is the basis of a number of important methods for estimating these hydrocarbons more especially in mixtures with other substances, e.g., in cracked gasoline. The halogens generally used for this purpose are bromine and iodine, the amount of halogen absorbed by the olefin being determined under standard conditions. The Hanus[2] method employs iodine while the McIlhiney[3] and Francis[4] methods are based on combination with bromine. The bromine is obtained by treating a bromide-bromate solution with dilute sulphuric acid. It is liberated slowly and absorbed by the olefin as fast as it is formed, thus avoiding substitution. Though these methods are excellent in their way, they all have certain disadvantages, among which may be mentioned the following:[5]

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[1] See Ingold and Ingold, *J.C.S.*, 1931, 2354, on the influence of substituents on the additive reactivity of ethylene derivatives.

[2] *Z. Nahr.-Genussm.*, 1901, 4, 913; *Chem. Soc. Abs.*, 1902, 82 (2), 112. Ingold and Smith, *J.C.S.*, 1931, 2742; Ingold and Ramsden, *J.C.S.*, 1931, 2746.

[3] *J.A.C.S.*, 1899, 21, 1084.

[4] *Ind. Eng. Chem.*, 1926, 18, 821.

(1) Frequently the theoretical absorption is not attained.
(2) The absorption depends upon the concentration of the reactants, upon the particular olefins under examination, and upon the time of reaction.
(3) Substitution reactions are exceedingly difficult to eliminate entirely.

Although a vast amount of work has been carried out on the preparation and properties of olefin halides, the quantity of really fundamental research on the mechanism of the process is surprisingly small.

According to Plotnikov[6] the union of ethylene and bromine to form the dibromide occurs instantaneously and completely at ordinary temperatures and the reaction only slackens to a measurable velocity at —100° C., at which temperature the reaction (in petroleum ether solution) was found to be of the second order. Stewart and Edlund,[7] on the other hand, found the combination of bromine (mixed with air) and ethylene in the gaseous state was slow at 0° C. though approximately 10 times as fast as the vapor-phase combination of ethylene and chlorine mixed with dry air at 17° C. In both instances the reaction was considered as being mainly a surface phenomenon,[8] which took place principally on the walls of the container. A very thorough examination of the relative rates of bromination of the olefins, particularly in carbon tetrachloride solution, has been made by Davis,[9] whose work has helped to clarify our ideas in this field. This investigator found that the rate of combination of ethylene and bromine in carbon tetrachloride in the dark depended greatly upon the quantity of moisture present in solution. When the reagents were very carefully dried the dark reaction was very slow, the second order reaction coefficient K being as low as 0.006 at 25° C. Bright light enormously increased the rate of bromination in dry carbon tetrachloride, while, remarkable to relate, the rate of bromination increased progressively as the temperature was reduced from 25° to 0° C. The phenomenal increase in the rate of reaction with the decrease in temperature was attributed to the reaction proceeding through the agency of a bromine hydrate and not by direct combination of ethylene and bromine. This hypothesis also explained the importance of small amounts of moisture in this reaction. Just as with ethylene, the bromination of propylene (dark reaction) in dry carbon tetrachloride was considerably faster at 0° C. than at 25° C., though, on the other hand, temperature changes seemed to have little influence on the rates of bromination of trimethylethylene and di-isobutylene. Davis studied the rate of bromination (dark reaction) of various olefins in dry carbon tetrachloride at 25° C. In Table 99 are given the *lowest* values obtained for the velocity coefficient K; the relative values are to be regarded as only qualitative.

TABLE 99.—*Velocity Coefficient of Bromination of Various Olefins.*

Olefin	K	Olefin	K
Ethylene	0.006	Butene-2 Isobutene	60.0
Propylene	0.2	Trimethylethylene	250.0
Butene-1	2.0	Di-isobutene	20.0

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[5] Howes, *J. Inst. Pet. Tech.*, 1929, **15**, 101.
[6] "Allgemeine Photochemie," W. deGruyter and Co., Berlin, 1920.
[7] *J.A.C.S.*, 1923, **45**, 1014. See also Stewart and Fowler, *J.A.C.S.*, 1926, **48**, 1187.
[8] Stewart and Fowler, *J.A.C.S.*, 1926, **48**, 1187.
[9] *J.A.C.S.*, 1928, **50**, 2769.

It will thus be seen that ethylene brominates at the slowest rate[10] while, of the olefins examined, trimethylethylene displayed the greatest reaction velocity. The reactivity of the simple monolefins thus appears to be at a maximum with the pentenes and their immediate homologues. A comparison of the rates of bromination of olefins in dry carbon tetrachloride in the dark and also when exposed to light showed that in the light the rates of reaction tend to show less divergency than in the dark. This interesting fact is brought out by the figures in Table 100, given by Davis, for the reaction coefficients, *K*, for ethylene, propylene, and di-isobutylene in the dark and the light, respectively.

TABLE 100.—*Velocity Coefficient of Bromination of Ethylene, Propylene and Di-isobutylene.*

	K Dark Reaction		*K* Light Reaction	
	Values	Ratios	Values	Ratios
Ethylene	0.01	1	2	1
Propylene	0.2	20	2.5	1.3
Di-isobutylene	20.0	2000	40.0	20.0

NOMENCLATURE OF HALOGENATED DERIVATIVES OF HYDROCARBONS

In the naming of addition products of unsaturated hydrocarbons some questions concerning their designation may arise. For example, dichloroethylene ($ClHC{=}CHCl$) may be easily confused with ethylene dichloride ($ClH_2C.CH_2Cl$). The former is an unsaturated compound, whereas the latter is completely saturated. In names such as "acetylene dichloride" the compound is less unsaturated than the hydrocarbon used for its designation. It does not contain an acetylene triple bond. The exact unsaturation of the compound is indicated more clearly by its other name, "dichloroethylene," which shows that it contains only a double bond. The naming of the halogenated compounds by means of the unsaturated hydrocarbon from which they are derived serves to emphasize their origin. Although to the chemist ethylene dichloride and 1,2-dichloroethane are the same material and both designations are equally acceptable, nevertheless, the name "ethylene dichloride" has been used to designate the compound made from ethylene by addition of chlorine, and "1,2-dichloroethane" to mean that made by substitution of chlorine for hydrogen atoms in ethane. Such distinctions are purely arbitrary, however. As the series of hydrocarbons is ascended and the structures of the derivatives become more complex, the halogen compounds can only be designated as derivatives of the hydrocarbon, preceded by a prefix indicating the nature and number of the halogen atoms.[10a] To avoid any confusion which may result Table 101 gives the known chlorinated products of the C_1 and C_2 hydrocarbons,[10b] from which the higher derivatives can be designated by analogy.

THE ETHYLENE DIHALIDES AND THEIR DERIVATIVES

Although ethylene reacts less rapidly with halogens than its immediate homologues, good yields of the dichloride and the dibromide may be readily obtained. These substances, especially the former, are assuming a position of some indus-

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[10] This is in agreement with the results of Suida and Wesely (*Z. anal. Chem.*, 1924, 64, 147) who state that ethylene reacts the slowest of the simple olefins toward bromine water.

[10a] *Cf.* Patterson, "Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry," *J.A.C.S.*, 1933, 55, 3914; Bernthsen-Sudborough, "Textbook of Organic Chemistry," D. Van Nostrand Co., Inc., New York, 1922, 58.

[10b] Some of these derivatives are discussed in later chapters (28, 29, and 30).

TABLE 101.—*Chlorinated Products of the C_1 and C_2 Hydrocarbons.*

Formula	Chemical Names	Other Names	Physical Properties[a] M.P. °C.	B.P. °C.	$D^{20°}_{4°}$
		Chlorinated Products of C_1-Hydrocarbons			
CH_3Cl	Chloromethane	Methyl chloride	−97.6	−23.7	0.920 ($^{18°}_{4°}$)
CH_2Cl_2	Dichloromethane	Methylene chloride	−96.7	40.1	1.336
$CHCl_3$	Trichloromethane	Methenyl chloride, Chloroform, Formyl trichloride	−63.5	61.2	1.489
CCl_4	Tetrachloromethane	Carbon tetrachloride, "Tetra," "Benzinoform," Perchloromethane	−23.0	76.8	1.595
		Chlorinated Products of C_2-Hydrocarbons			
CH_3CH_2Cl	Chloroethane	Ethyl chloride, Hydrochloric ether,	−138.7	12.2	0.910
CH_3CHCl_2	1,1-Dichloroethane	Ethylidene chloride	−96.7	57.3	1.174
$CH_2Cl.CH_2Cl$	1,2-Dichloroethane	Ethylene dichloride, Ethylene chloride, Oil of the Dutch chemists	−35.3	83.7	1.257
$CH_3.CCl_3$	1,1,1-Trichloroethane	Methylchloroform		74.1	1.334
$CH_2Cl.CHCl_2$	1,1,2-Trichloroethane	Trichloroethane	−36.7	113.5	1.443
$CH_2Cl.CCl_3$	1,1,1,2-Tetrachloroethane	Tetrachloroethane		130.5	1.588
$CHCl_2.CHCl_2$	1,1,2,2-Tetrachloroethane	Acetylene tetrachloride, "Acetosol," "Boroform," "Cellon"	−43.8	146.3	1.600
$CHCl_2.CCl_3$	1,1,2,2,2-Pentachloroethane	Pentachloroethane	−29.0	162	1.709 ($^{0°}_{4°}$)
$CCl_3.CCl_3$	1,1,1,2,2,2-Hexachloroethane	Perchloroethane, Carbon hexachloride, Carbon trichloride,	185	185	
$H_2C{=}CHCl$	Chloroethene	Chloroethylene, Vinyl chloride		−15	
$H_2C{=}CCl_2$	1,1-Dichloroethene	*asym.- or α,α-* Dichloroethylene	50	37	
$ClHC{=}CHCl$	1,2-Dichloroethene	*sym.- or α,β-* Dichloroethylene, Acetylene dichloride	*cis* −50	48.4	1.265 ($^{15°}_{4°}$)
			trans −80.5	60.3	1.291 ($^{15°}_{4°}$)
$ClHC{=}CCl_2$	1,2,2-Trichloroethene	Trichloroethylene, "Chlorylene," "Westrosol," "Tri"	−86.4	88	1.477
$Cl_2C{=}CCl_2$	1,1,2,2-Tetrachloroethene	Tetrachloroethylene, Perchloroethylene, Carbon dichloride, "Westron"	−22.4	120.8	1.623
$HC{\equiv}CCl$	Chloroethyne	Chloroacetylene			
$ClC{\equiv}CCl$	Dichloroethyne	Dichloroacetylene	−50		

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[a] Values principally from "International Critical Tables," National Research Council, McGraw-Hill Book Co., Inc., New York, 1926; and Beilstein, "Handbuch der organischen Chemie," J. Springer, Berlin, 1918.

trial importance. Iodine reacts slowly with ethylene in direct sunlight at about 60° C.,[11] but this reaction does not as yet appear of technical interest. The fluorine derivatives of the lower olefins have been little investigated and offer a very promising field of research.

ETHYLENE DICHLORIDE (1,2-DICHLOROETHANE)

Ethylene dichloride, $ClCH_2{\cdot}CH_2Cl$, is a heavy colorless liquid with a chloroform-like odor and having the following physical characteristics:—boiling point 83.5° C. at 760 mm.; freezing point —36° C.; d^{20}_4 1.2569; d^0_4 1.2824; n^{20} 1.444; viscosity at 25° C., 0.78 centipoises; vapor pressure at 20° C. 61.6 mm.; specific heat at 30° C. 0.3054 calories per gram; surface tension at 25° C., 37.5 dynes per sq. cm.; closed cup flash point, 58° F.; apparent ignition temperature in air, 499° C.; latent heat of evaporation at 82.2° C., 77.34 calories per gram.[12]

Ethylene dichloride is practically insoluble in water, sparingly soluble in alcohol and ether, and miscible with ethereal oils, fats, and mineral oils generally. It is one of the most stable of the commonly available chlorinated hydrocarbons and may be handled in the presence of water at its boiling point without danger of corrosion to metal apparatus. Besides its stability to hot water it is also resistant to oxidation. Although ethylene dichloride will burn, this substance is on the border line between inflammable and non-inflammable solvents and ethylene dichloride flames are readily extinguished. Its lower explosive limit in air is 6.2 per cent compared with 1.4 per cent for benzene and about 1.5 per cent for ordinary gasoline.[12] Exposure to light is said to promote decomposition and hydrolysis but the addition of 1 or 2 per cent of alcohol increases its stability.

Ethylene dichloride was first prepared about 1795 by four Dutch chemists, Delman, Bondt, van Troostwyk, and Lauwerenburgh,[13] by the action of chlorine on ethylene, hence this substance became known under the name of "Dutch Liquid." Since that time this compound has been the subject of a number of academic investigations but it was not available in quantity and at low price until about 1927. In order to prepare this material cheaply, an abundant and cheap supply of both chlorine and ethylene (the latter, for example, from vapor-phase cracking of petroleum) is essential.

The scientific work carried out on the chlorination of ethylene indicates that combination in the dry state and in the vapor phase at ordinary temperatures only occurs slowly.[14] The reaction may apparently be speeded up by working in the liquid phase, by the use of catalysts, by employing a solvent, or by using higher temperatures, but it is very difficult to limit the reaction to direct addition since substitution also occurs readily especially at higher temperatures. Doroganevskaja [15] has indicated that gaseous chlorine and ethylene do not combine in the absence of a catalyst. In glass vessels reaction takes place due to the catalytic effect of the glass itself, and the reaction can be further accelerated by the addition of ethylene dichloride. Under the proper conditions, such as concentration or velocity of the gases, yields of ethylene dichloride as high as 93.6 per cent can be obtained. Moreover, the addition reaction is highly exothermic and the heat liberated in this process, unless rapidly absorbed, tends to promote substitution reactions. Thus Smythe[16] found that ethylene and chlorine reacted very readily in the presence of calcium chloride as catalyst, so much heat being generated that the apparatus had to be cooled during the operation. The chlorinated product contained about 50 per cent of ethylene dichloride, 25 per cent of trichloroethane, and 25 per cent of higher-boiling products, probably polyhalogenated derivatives.

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[11] Faraday, *Annals of Philosophy*, 1820, **18**, 118; Reynault, *Ann. chim.*, 1835, **2**, 59; *Ann. chim. phys.*, 1835, **59**, 367.

[12] Fife and Reid, *Ind. Eng. Chem.*, 1930, **22**, 513.

[13] *Crells Annalen*, 1795, **2**, 200.

[14] See Gersdorff, "A Bibliography of Ethylene Dichloride," *U. S. Dept. Agriculture, Misc. Publ.* 117, 1932. The properties, technology and value of dichloroethane are also reviewed by Zimakov, *J. Chem. Ind. (Moscow)*, 1932, No. 6, 36; *Chem. Abs.*, 1932, **26**, 5290.

[15] *J. Chem. Ind. Russia*, 1931, **8**, 857; *Brit. Chem. Abs.* **B**, 1931, 962.

According to the observations of Stewart and Smith,[17] under certain circumstances the vapor-phase combination of chlorine with ethylene leads to a quantitative formation of ethylene dichloride while, under other conditions, only 1,2,2-trichloroethane and hydrogen chloride are formed. The substitution reaction is induced by the addition reaction, the heat of formation of ethylene dichloride being utilized to promote the formation of trichloroethane. In the absence of moisture and light the reactions are autocatalytic, while the presence of oxygen inhibits the utilization of the reaction energy to promote substitution, i.e., suppresses the substitution reaction. Nitrogen and moisture have little effect. Bahr and Zieler[18] have observed that, in the absence of catalysts, ethylene dichloride is formed from ethylene and chlorine in 90 per cent yield at —20° to —30° C. Lower temperatures do not increase the yield, while at higher temperatures the yield is decreased. Trichloroethane is formed in increasing amount with rising temperature and constitutes the main product at ordinary temperatures. The amount of tetrachloroethane formed, though always small, increases with rising temperature. According to Bahr and Zieler, the higher chlorinated products are not produced by subsequent action of chlorine on ethylene dichloride but by direct action of chlorine on ethylene. The course of the reaction was found to depend mainly on the temperature and not on the relative proportions of the reactants.

A number of processes dealing with the production of ethylene dichloride from ethylene and chlorine have been developed; in many of these, however, it is possible that the products are contaminated to some extent by higher chlorinated substances.

Tinker[19] made olefin dichlorides by passing cracking gas, chlorine, and a cold inert liquid (e.g., ethylene dichloride) through a reaction tower. The products pass to a condenser which removes the olefin dihalides, leaving a gas consisting mainly of paraffins. Vapor-phase chlorination of gaseous olefins to produce olefin dichlorides at 50° to 150° C. in the absence of steam or water and in the presence of contact substances such as brick, pumice, sand, coke, charcoal, ferric oxide, alumina, or magnesia is suggested by Harding.[20] The products are said to be practically free from higher substitution compounds. Bergius[21] described the use of coal gas, or the gaseous products obtained from the distillation of carbonaceous matter (lignite or oils), as a source of ethylene for the manufacture of ethylene dichloride by vapor-phase catalytic chlorination, followed by compression and cooling to separate the ethylene dichloride. Chlorination is said to take place in the presence of porous charcoal, with or without the addition of a halogen carrier, such as chlorides of antimony, sulphur, or phosphorus.[22]

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[16] *Gas J.*, 1920, 149, 691; *J.S.C.I.*, 1920, 39, 312A.

[17] *J.A.C.S.*, 1929, 51, 3082.

[18] *Z. angew. Chem.*, 1930, 43, 233; *Brit. Chem. Abs.* A, 1930, 572. See also Kinumaki, *J. Chem. Soc. Japan*, 1933, 54, 142; *Chem. Abs.*, 1933, 27, 2369.

[19] British Patent 108,602, 1916; *Chem. Abs.*, 1917, 11, 3428.

[20] British Patent 126,511, 1918; *J.S.C.I.*, 1919, 38, 513A.

[21] British Patents 147,908 and 147,909, 1920; assigned to T. Goldschmidt A.-G.; *Chem. Abs.*, 1921, 15, 97. Also German Patent 298,931, 1921. The catalysts specified for this process are the chlorides of iron, copper or antimony.

[22] Farbenfabriken vorm. F. Bayer and Co., British Patent 177,362, 1921; *Chem. Abs.*, 1922, 16, 3093.

It is stated that natural magnesite, which has been heated for some time at 400° to 500° C., is a catalyst for chlorination reactions, particularly the chlorination of ethylene to the dichloride.[23]

In the process developed by the T. Goldschmidt A.-G.[24] a mixture of ethylene and chlorine, with the ethylene in excess, is passed over catalysts at temperatures of 30° to 120° C. in such a manner that the ethylene dichloride formed is rapidly removed from the reaction zone. Askenasy and Heller[25] have recommended that the reaction between ethylene and chlorine take place in the presence of lead, as a catalyst, and that the temperature of the reaction zone be kept below 100° C.

Among the more interesting processes are those of Curme[26] who described the production of ethylene dichloride by mixing dry ethylene with liquid chlorine at a temperature below 0° C. and at a pressure corresponding to the vapor pressure of chlorine. At higher temperatures higher chlorinated substances are said to be formed. It is understood that the process, which appears to be equally simple and efficient, is one which has been employed for large-scale production of ethylene dichloride. According to Maier[27] ethylene dichloride is produced by bringing together ethylene and chlorine, both of which have been previously cooled to a low temperature, for example —30° C. The reaction velocity between gaseous ethylene and liquid chlorine (at —78° C.) is almost proportional to the partial pressure of the ethylene.[28] Backhaus[29] described a process for preparing pure dihalide by passing a mixture of an olefin and a halogen, e.g., chlorine and ethylene, in a continuous stream through cooled tubes while continuously returning the uncombined gases to the stream entering the tubes.[30]

A two-stage process for making ethylene dichloride consists in first allowing ethylene to react with an insufficient amount of chlorine (both in the gaseous phase) for complete reaction and second completing the chlorination by the use of a saturated solution of chlorine in liquid chlorohydrocarbons.[31]

Ernst and Wahl[32] utilized chlorine produced *in situ* by the oxidation of hydrogen chloride. The process, which is a continuous one, may be summarized in the equation:

$$2C_2H_4 + 4HCl + O_2 = 2C_2H_4Cl_2 + 2H_2O$$

For example, a mixture of 100 volumes of air, about 20 volumes of ethylene and at least 40 volumes of hydrogen chloride is passed through an acid-resisting contact chamber containing lumps of pumice soaked with cupric chloride and maintained at 300° C. Besides ethylene dichloride, only traces of other chlorinated hydrocarbons are formed. The use of active charcoal, saturated with sulphur chloride, as a catalyst for the combination of ethylene and chlorine to yield ethylene dichloride has been proposed by Wietzel and Dierksen.[33]

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[23] Fritzweiler, Stuer and Grob, German Patent 469,552, 1925; assigned to Kali-Chemie A.-G.; *Chem. Abs.*, 1929, **23**, 1728.

[24] German Patent 298,931, 1921.

[25] U. S. Patent 1,851,970, Apr. 5, 1932; *Chem. Abs.*, 1932, **26**, 2989.

[26] U. S. Patents 1,315,542 and 1,315,545, Sept. 9, 1919; assigned to Union Carbide Co.; *J.S.C.I.*, 1919, **38**, 847A. Also, *Chem. Met. Eng.*, 1921, **25**, 999.

[27] French Patent 653,434, 1928; *Chem. Abs.*, 1929, **23**, 3718; German Patent 529,524, 1927; *Chem. Abs.*, 1931, **25**, 5178.

[28] Kinumaki and Mitsukuri, *J. Chem. Soc. Japan*, 1932, **53**, 398; *Chem. Abs.*, 1932, **26**, 4231.

[29] U. S. Patent 1,402,337, Jan. 3, 1922; assigned to U. S. Industrial Alcohol Co.; *Chem. Abs.*, 1922, **16**, 934.

[30] U. S. Patent 1,402,338, Jan. 3, 1922; assigned to U. S. Industrial Alcohol Co.; *Chem. Abs.*, 1922, **16**, 934.

[31] Matisen, Russian Patent 24,877, 1932; assigned to Gosudarstvennuii Trest Rezinovoi Promuishlennosti; *Chem. Abs.*, 1932, **26**, 3513.

[32] German Patent 430,539, 1922; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1926, 900.

[33] German Patent 420,500, 1923; *Brit. Chem. Abs.* **B**, 1926, 464; see also Dierksen and Schlecht, German Patent 409,181, 1923; *J.S.C.I.*, 1925, **44**, 448B; both patents assigned to Badische Anilin- und Soda-Fabrik.

Mersereau[34] has described a method of treating olefins, or diolefins, with chlorine in a (dark) tower down which a shower of cooled water or chlorinated hydrocarbons is allowed to flow. When pure chlorine is used and water is employed to control the temperature, the most desirable reaction temperature is 15° C. The apparatus suggested by Mersereau consisted essentially of a vertical reaction tower, the lower end of which is placed in a container employed to collect the water and the chlorinated products. Both chlorine and ethylene are introduced at the bottom of the tower through perforated openings to secure good mixing, and reaction takes place as the gaseous mixture travels upwards. Cold water is sprayed into the top of the tower. Water and chlorinated products are retained in the container at the bottom of the tower, and because of their wide differences in densities readily separate into two layers which can be withdrawn separately. The gaseous products leave the top of the reaction tower through a condenser. Any condensate formed is allowed to flow from the bottom of the condenser to the container at the bottom of the reaction tower.

Strosacker[35] has pointed out that the dichloride of ethylene, or of other olefins, may be obtained by passing the olefin, in the gaseous state, through a spray of antimony pentachloride dissolved in ethylene dichloride. Only addition compounds are said to be formed, no substitution reactions taking place. The chlorination of ethylene in an atmosphere consisting of the vapors of halogenated hydrocarbons containing a halogen of higher atomic weight than chlorine, as for example ethylene dibromide, has been described by Dow.[36]

Summarizing, it may be said that in order to obtain pure ethylene dichloride by the chlorination of ethylene and fairly free from substitution derivatives, it is necessary to maintain the reaction mixture at a fairly low temperature. Among the best methods of carrying out this reaction on an industrial scale is by passing cooled ethylene into cooled liquid chlorine at a low temperature in the absence of catalysts.

When ethylene is treated with dilute hypochlorous acid, ethylene chlorohydrin is produced almost exclusively, but in the case of the higher homologues of ethylene considerable amounts of olefin dichloride are simultaneously formed with the chlorohydrin.

OTHER METHODS FOR THE PRODUCTION OF ETHYLENE DIHALIDES

Ethylene dihalides may be produced, according to Bauer,[37] by the direct addition of two molecules of hydrogen halide to acetylene at ordinary temperatures in the presence of a gaseous oxidizing agent such as air, oxygen, nitrogen, peroxide, formaldehyde, formic acid or iodine. The corresponding dihalide is said to be rapidly formed in a yield of 90 per cent. The reaction may be represented thus:

$$CH\equiv CH + 2HX \longrightarrow CH_2XCH_2X$$

Although on the basis of former work the opinion has been expressed[38] that the addition of two molecules of halogen acid to acetylene leads to the production of the 1,1-dihalogenoethane exclusively, other work[39] has shown that both the 1,1- and the 1,2-ethylene dihalides are produced. Wibaut[40] has very thoroughly examined this reaction in the case of hydrogen bromide and acetylene and found that, though a mixture of the two dibromoethanes was produced, reasonably good yields of ethylene dibromide (1,2-dibromoethane) could be obtained using certain metallic chlorides on asbestos as catalysts. Evidently, therefore, the direct addition of hydrogen chloride to acetylene to yield ethylene dichloride is entirely possible, provided the correct conditions can be found.

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[34] U. S. Patent 1,509,603, Sept. 23, 1924; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1925, 19, 168.

[35] U. S. Patent 1,754,656, Apr. 15, 1930; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* B, 1931, 621.

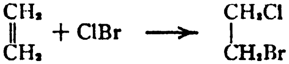
[36] U. S. Patent 1,841,279, Jan. 12, 1932; assigned to Dow Chemical Co.; *Chem. Abs.*, 1932, 26, 1615.

[37] U. S. Patent 1,540,748, June 9, 1925; *J.S.C.I.*, 1925, 44, 692B; U. S. Patent 1,414,852, May 2, 1922; *Chem. Abs.*, 1922, 16, 2150; both patents assigned to Röhm and Haas A.-G. Also German Patents 368,467, 1922, and 394,194, 1929.

[38] Meyer-Jacobson, "Lehrbuch der organischen Chemie," 1913, II, 27.

It has also been reported that ethylene dichloride[41] may be produced by the direct chlorination of ethane in the presence of activated carbon and over a temperature range from 100° to 300° C. At the same time, however, ethylidene chloride (in quantities equivalent to the ethylene dichloride) and some 1,1,1-trichloroethane are formed.

In this connection it is interesting to note that when ethylene is allowed to react with an equimolecular mixture of chlorine and bromine (presumably the compound ClBr), 1-chloro-2-bromoethane is the main product in the cold.[42]



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ClBr \longrightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2Br \end{matrix}$$

According to Dow,[43] when ethylene is allowed to react with a gaseous mixture of equal atomic proportions of chlorine and bromine (obtained by bubbling chlorine through liquid bromine at 15° to 20° C.), 1-chloro-2-bromoethane is readily formed.

Uses of Ethylene Dichloride

Ethylene dichloride is a substance which can be produced in large quantities, and will probably find a number of varied applications. Already it has been suggested as a solvent, as a fumigant, as an ingredient in the manufacture of lacquers and especially in the synthesis of ethylene glycol or its derivatives.

As a solvent ethylene dichloride possesses many desirable characteristics, as for example its low cost, high solvent power, low inflammability, and availability in large quantities.[44] It is an excellent solvent for many fats, oils and resins, but will not dissolve cellulose nitrate or acetate except after being mixed with certain other solvents. A mixture containing 70 to 80 per cent of ethylene dichloride and 20 to 30 per cent of methyl or ethyl alcohol is said to possess a high solvent power for cellulose acetate.[45] Other proposed uses which involve its solvent powers are as an extracting agent in the manufacture of vegetable oils; in the separation of mineral oils from paraffin wax,[46] the latter substance being only slightly soluble in this solvent at temperatures below 25° C.; as a dry cleaning agent, either alone[47] or admixed with other chlorinated hydrocarbons, such as carbon tetrachloride or propylene dichloride.[48] Ethylene dichloride is cheaper than carbon tetrachloride on a volumetric basis and superior in its stability toward water and steam.[49]

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[39] Reboul, *Ann.*, 1870, **155**, 30; *Ann. chim. phys.*, 1878 (5), **14**, 470.

[40] *Rec. trav. chim.*, 1931, **50**, 314; *Chem. Abs.*, 1931, **25**, 2684.

[41] Müller-Cunradi, German Patent 436,999, 1921; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1927, 428.

[42] Delépine and Ville, *Bull. soc. chim.*, 1920, **27**, 673; *Chem. Abs.*, 1920, **14**, 3405.

[43] U. S. Patent 1,306,472, June 10, 1919; *Chem. Abs.*, 1919, **13**, 2040.

[44] According to Durrans ("Solvents," Chapman and Hall, London, 1930), however, ethylene dichloride is toxic and produces dangerous physiological effects similar to those of chloroform.

[45] Frazier and Reid, *Ind. Eng. Chem.*, 1930, **22**, 604.

[46] Livingston, U. S. Patent 1,848,636, March 8, 1932; assigned to Gulf Refining Co.; *Chem. Abs.*, 1932, **26**, 2860.

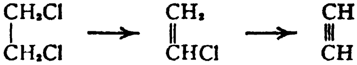
[47] Fife and Reid, *Ind. Eng. Chem.*, 1930, **22**, 513.

[48] Putnam and Poffenberger, U. S. Patent 1,817,582, Aug. 4, 1931; assigned to Dow Chemical Co.; *Chem. Abs.*, 1931, **25**, 5581. Warrington, *Can. Chem. Met.*, 1932, **16**, 39; *Chem. Abs.*, 1932, **26**, 2601.

Frazier and Reid[50] have discussed the use of ethylene dichloride in the manufacture of lacquers. Its advantages appear to be resistance to hydrolysis in the presence of water and low inflammability. Its disadvantage is the fairly high rate of evaporation which necessitates the addition of a higher-boiling solvent as a "leveller".

When employed as a fumigant it is often mixed with carbon tetrachloride to render it non-inflammable, approximately 25 per cent by volume of carbon tetrachloride being sufficient. A number of tests with a 3:1 mixture of ethylene dichloride and carbon tetrachloride on grain, flour, food and seeds has been recorded by Hoyt.[51] According to Russ[52] both ethylene dichloride and ethylene oxide are highly toxic to insects but relatively non-toxic to man.

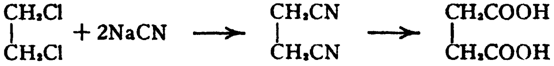
The conversion of ethylene dichloride to ethylene glycol, by hydrolysis with aqueous sodium carbonate, or to glycol diacetate, by heating with an anhydrous salt of acetic acid, is discussed in Chapter 22. When heated with caustic alkalies ethylene dichloride loses first one molecule of hydrogen chloride to yield vinyl chloride. The properties and uses of this latter compound are mentioned in Chapter 28. Further treatment with caustic alkalies eventually yields acetylene, thus:



$$\begin{array}{c}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH_2Cl}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CHCl}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array}$$

A similar series of changes occurs when ethylene dichloride is subjected to pyrolysis at 600° C. in an atmosphere of nitrogen, vinyl chloride and hydrogen chloride being produced[53] (this reaction is probably reversible at lower temperatures), while at still higher temperatures acetylene is produced.

Ethylene dichloride may also be employed for the manufacture of succinic acid. Condensation with sodium cyanide produces succinonitrile, which may be readily hydrolyzed by means of hydrochloric acid to yield succinic acid, thus:



$$\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH_2Cl}\end{array} + 2\mathrm{NaCN} \longrightarrow \begin{array}{l}\mathrm{CH_2CN}\\ |\\ \mathrm{CH_2CN}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2COOH}\\ |\\ \mathrm{CH_2COOH}\end{array}$$

The condensation of ethylene dichloride and sodium cyanide is very conveniently effected by heating in the presence of succinonitrile itself.[54] This replacement of the chlorine atoms in ethylene dichloride by other groups may be accomplished occasionally in a single step. For example, in making ethylene dithiocyanate, sodium thiocyanate in the dissolved form and chlorine are allowed to react with ethylene.[55] This reaction is said to be applicable also to the homologues of ethylene.

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[49] Killeffer, *Ind. Eng. Chem.*, 1927, 19, 636. The addition of a small proportion of arylamines or phenols is said to stabilize dichlorides (The Roessler and Hasslacher Chemical Co., French Patent 732,569, 1932; *Chem. Abs.*, 1933, 27, 304).

[50] *Loc. cit.*

[51] *Ind. Eng. Chem.*, 1928, 20, 931.

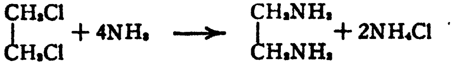
[52] *Ind. Eng. Chem.*, 1930, 22, 844. Also, Roark, *Ind. Eng. Chem.*, 1932, 24, 646.

[53] See, Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., 1929, 131. *Cf.* Baxter, Edwards and Winter, British Patent 363,009, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1932, 331.

[54] Wheeler, British Patent 333,989, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1930, 1058.

[55] Kauffmann, U. S. Patent 1,859,399, May 24, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 3804.

Ethylenediamine may be produced from ethylene dichloride by interaction with ammonia according to the equation



$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + 4NH_3 \longrightarrow \begin{matrix} CH_2NH_2 \\ | \\ CH_2NH_2 \end{matrix} + 2NH_4Cl$$

Thus on heating ethylene dichloride with 33 per cent aqueous ammonia for 5 hours in an autoclave at 115° to 120° C., a good yield of ethylenediamine is obtained.[56] Ethylenediamine is an oily base of melting point 8.5° C., boiling point 116.5° C. at 760 mm. and d^{15}_{4} 0.902.

The reaction between ethylene dichloride and ammonia at high temperatures and under pressure can be made to yield polyethylene polyamines which have been recommended as rubber vulcanization accelerators.[57] It is stated that this procedure effects both condensation and polymerization.

Chloroethylsulphuryl chloride can be prepared by treating ethylene dichloride with fuming sulphuric acid (60 to 65 per cent SO_3) in the cold. On diluting with water the chloroethylsulphuryl chloride separates as a colorless heavy oil with an odor like that of formaldehyde and a boiling point of 120° to 122° C. at 80 mm. The yield is good but not quantitative since a certain amount of dichlorethyl sulphate, a colorless oil, boiling point 180° to 182° C. at 60 mm., is also formed.[58]

Ethylene dichloride reacts with metal sulphites in ethyl or methyl alcohol to yield salts of chloroethanesulphonic acid,[58a] from which the acid chloride may be obtained. Catalysts for the reaction are copper, copper sulphate, and barium chloride.

The production of plastic materials by the interaction of ethylene dichloride and the polysulphides of alkali or alkaline earth metals has been described by Patrick and Mnookin.[59] These products resemble soft rubber, and are characterized by a high sulphur content and insolubility in organic solvents except carbon disulphide. They also possess vulcanizing properties, and can be incorporated with unvulcanized rubber and the mixture subjected to vulcanization.

The plastic materials, being rubber-like, may be compounded and vulcanized like rubber itself. The product so obtained is insoluble in organic solvents, particularly petroleum distillates, and can be used, for example in the form of hose, for the handling of these solvents. Another use is in electrical insulation.

Baer[60] also has made plastic materials by the reaction between chlorinated hydrocarbons, such as ethylene dichloride, and the alkali or alkaline earth sulphides. Such materials are capable of being milled, compounded, molded or vulcanized like rubber itself. Another method of producing rubber-like substances is by the interaction of the chlorinated derivatives of unsaturated hydrocarbons, such as isoprene, and alkali and alkaline earth sulphides.[61]

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[56] Kraut, *Ann.*, 1882, **212**, 253. Fargher, *J.C.S.*, 1920, **117**, 1351. *Cf.* Curme and Lommen, U. S. Patent 1,832,534, Nov. 17, 1932; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1932, **26**, 999.

[57] Cadwell, British Patent 347,955, 1929; assigned to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, **26**, 2893.

[58] Ott, German Patent 374,141, 1920; assigned to Chemische Fabrik Weiler-ter Meer; *J.S.C.I.*, 1923, **42**, 1201A.

[58a] I. G. Farbenindustrie A.-G., British Patent 360,558, 1930; *Chem. Abs.*, 1933, **27**, 1006.

[59] Patrick, U. S. Patent 1,890,191, Dec. 6, 1932; *Chem. Abs.*, 1933, **27**, 1724; British Patent 350,472, 1930; *Chem. Abs.*, 1933, **27**, 450; British Patents 354,310 and 354,394, 1930; *Brit. Chem. Abs.* **B**, 1931, 936; British Patent 359,000, 1929; *Chem. Abs.*, 1932, **26**, 4981; British Patent 360,890, 1930; *Chem. Abs.*, 1933, **27**, 1114; British Patent 369,097, 1930; *Chem. Abs.*, 1933, **27**, 2260; French Patent 656,114, 1928; *Chem. Abs.*, 1929, **23**, 4030; French Patent 691,743, 1930; *Chem. Abs.*, 1931, **25**, 1412; French Patent 706,155, 1930; *Chem. Abs.*, 1932, **26**, 267; French Patent 719,212, 1931; *Chem. Abs.*, 1932, **26**, 3344; Canadian Patents 320,090, 320,091, 320,092, 1932; *Chem. Abs.*, 1932, **26**, 2621; German Patent 554,112, 1930; *Chem. Abs.*, 1932, **26**, 5183; German Patent 554,897, 1930; *Chem. Abs.*, 1932, **26**, 6080; Mnookin, British Patent 350,456, 1930; *Chem. Abs.*, 1932, **26**, 5392; Patrick and Mnookin, U. S, Patent 1,854,423, Apr. 19, 1932; *Chem. Abs.*, 1932, **26**, 3408; U. S. Patent 1,854,480, Apr. 19, 1932; *Chem. Abs.*, 1932, **26**, 3312; U. S. Patent 1,890,231, Dec. 6, 1932; *Chem. Abs.*, 1933, **27**, 1784; British Patent 302,270, 1927; *Chem. Abs.*, 1929, **23**, 4307; British Patent 350,549, 1930; *Chem. Abs.*, 1933, 27, 443.

[60] U. S. Patent 1,912,962, June 6, 1933; *Chem. Abs.*, 1933, **27**, 4247; British Patent 279,406, 1926; *Chem. Abs.*, 1928, **22**, 2856; British Patent 298,889, 1928; *Brit. Chem. Abs.* **B**, 1929, 652; British Patent 300.200, 1927; *Chem. Abs.*, 1929, **23**, 3548; British Patent 302,399, 1927; *Chem. Abs.*, 1929, **23**, 4376; British Patent 345,175, 1929; *Chem. Abs.*, 1933, **27**, 442; German Patent

The preparation of factice or sulphuretted oil products, which are soluble in hydrocarbons, by heating equal weights of a vegetable oil, e.g., rape seed oil, and a caoutchouc-like body, made from ethylene dichloride and alkali polysulphides, has been described by Baer.[62] The same rubber-like products can also be dissolved in carbon disulphide and mixed with rubber latex.[62a]

Some other uses which have been proposed for ethylene dichloride are: (a) as one of the components of a solvent for the polymerization of butadiene by means of sodium[63]; (b) for the production of cellulose ethers or as one of the components of mixed solvent for such ethers[64]; (c) together with isopropyl ether, acetone, propylene dichloride and chlorinated naphthalene as a composition for the removal of carbon in internal-combustion engines.[65]

TRICHLORO- AND TETRACHLOROETHANE

Two general types of reactions can be used in the preparation of these compounds as well as higher chlorinated derivatives. These reactions may be classified as (a) the further chlorination of lower chlorinated derivatives, or (b) the action of chlorine on unsaturated hydrocarbons, particularly acetylene, as in the case of tetrachloroethane.[66]

1,1,2-Trichloroethane, for example, can be prepared by the reaction between chlorine gas and ethylene dichloride at a temperature of about 60° C. and in the presence of such catalysts as antimony, iron or manganese.[67] This same compound may be obtained by allowing chlorine and ethylene to react at 30° C. and using a metal, such as copper, as a catalyst.[68] Vinyl chloride and chlorine are said to yield 1,1,2-trichloroethane when allowed to react at temperatures of 100° C. to 250° C. in the absence of a solvent and of light.[69]

Other methods for producing both 1,1,2-trichloro- and 1,1,2,2-tetrachloroethane involve the reaction between acetylene and either chlorine or a mixture of chlorine and hydrogen chloride. A discussion of these will be found in Chapter 28.

1,1,2-Trichloroethane is a colorless liquid boiling at 114° C. and having d^0_0 1.4784. It is practically insoluble in water, but miscible in all proportions with alcohol or

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530,734, 1928; *Chem. Abs.*, 1932, **26**, 329; Swiss Patent 127,540; Swiss Patent 132,325, 1927; *Chem. Abs.*, 1929, **23**, 5054; Swiss Patents 132,505, 132,506, 132,507, 132,508, 1926; *Chem. Abs.*, 1929, **23**, 5062; Swiss Patents 132,509, 132,510, 132,511, 132,512, 132,513, 132,514, 132,515, 1926; *Chem. Abs.*, 1930, **24**, 528.

[61] Baer, U. S. Patent 1,922,923, Aug. 15, 1933; *Chem. Abs.*, 1933, **27**. 5217; British Patent 314,524, 1928; *Chem. Abs.*, 1930, **24**, 1545; German Patent 526,121, 1928; *Chem. Abs.*, 1931, **25**, 4443; Swiss Patent 142,456, 1929; *Chem. Abs.*, 1931, **25**, 2332.

[62] U. S. Patent 1,828,587, Oct. 20, 1931; *Chem. Abs.*, 1932, **26**, 867; British Patent 313,917, 1928; *Chem. Abs.*, 1930, **24**, 1249; Swiss Patent 137,477, 1928; *Chem. Abs.*, 1930, **24**, 4426; Swiss Patents 142,354, 142,355, 142,356, 142,357, 1928; *Chem. Abs.*, 1931, **25**, 2332.

[62a] Baer, U. S. Patent 1,869,734, Aug. 2, 1932; *Chem. Abs.*, 1932, **26**, 5453; British Patent 345,175, 1929; *Chem. Abs.*, 1933, **27**, 442; French Patent 697,641, 1930; *Chem. Abs.*, 1931, **25**, 3199.

[63] I. G. Farbenindustrie A.-G., British Patent 347,802, 1930; *Chem. Abs.*, 1932, **26**, 2893.

[64] Ascherl and Gruber, German Patent 541,146, 1928; assigned to Alexander Wacker, Ges. für Elektrochem. Ind. G.m.b.H.; *Chem. Abst.*, 1932, **26**, 2052.

[65] Johnsen, U. S. Patent 1,850,881, March 22, 1932; *Chem. Abs.*, 1932, **26**, 2851.

[66] For a review of the methods of preparation of tetrachloroethane and trichloroethylene see Miloslavskii and Postovskii, *J. Ind. Chem.* (*Moscow*), 1930, 7, 1414; *Chem. Abs.*, 1931, **25**. 5391.

[67] Jung and Zimmermann, German Patent 545,993, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3520.

[68] Askenasy and Heller, German Patent 549,341, 1930; *Chem. Abs.*, 1932, **26**, 3887.

[69] Ernst and Lange, U. S. Patent 1,833,358, Nov. 24, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 1301. Also, U. S. Patent 1,833,393, Nov 24, 1931, for carrying out this reaction at lower temperatures.

ether. 1,1,2,2-Tetrachloroethane is a colorless liquid possessing an odor much like that of chloroform. It boils at 147° C. and has d_0^0 1.614. Its miscibility with other liquids is similar to that of 1,1,2-trichloroethane.

These two liquids appear to be somewhat less stable than ethylene dichloride. In the presence of moisture they are stable in contact with either tin or lead; other metals, however, slowly reduce them, under the same conditions, to the respective ethylene derivatives containing one less chlorine atom. Their uses are similar to those of ethylene dichloride as they are solvents, either alone or mixed with other liquids, for many substances such as fats, oils, waxes, cellulose esters or resins. As an example, in the preparation of an insecticide either chrysanthemum or derris root is extracted with a mixture containing 67.6 per cent trichloroethane and 32.4 per cent methyl alcohol. Evaporation of the solvent leaves a residue which may be used in the production of insecticides.[70] Tetrachloroethane has been suggested also as a component of soap compositions.[71]

HEXACHLOROETHANE

Mention should be made of a substance which may be readily obtained by chlorinating ethylene with an excess of chlorine, namely hexachloroethane, C_2Cl_6. Miller[72] found this substance could be readily produced by passing ethylene mixed with a slight excess of chlorine through a pyrex tube packed with activated charcoal at 300° to 350° C. A 10 per cent excess of chlorine over and above that required for the reaction, $C_2H_4 + 5Cl_2 \rightarrow C_2Cl_6 + 4HCl$, suppresses the formation of lower chlorinated products and with a flow of 60 cc. of ethylene per minute over 200 grams of charcoal a conversion of 80 to 90 per cent of the theoretical was obtained.

Hexachloroethane may be prepared also by passing acetylene into a boiling mixture of sulphur chloride. The yield may then be further increased by leading alternate streams of chlorine gas and acetylene into this mixture.[73] Tetrachloroethane may be converted to hexachloroethane very rapidly and almost quantitatively by the action of chlorine in the presence of light from either an open arc lamp or a mercury vapor lamp. Pentachloroethane may be obtained as an intermediate product if the reaction is stopped when about 10 per cent excess chlorine (over that required for the pentachloride) has been added.[74]

ETHYLENE DIBROMIDE (1,2-DIBROMOETHANE)

Ethylene dibromide may be readily prepared[75] by passing ethylene through cooled bromine or bromine and water, the latter being often added to prevent evaporation of the bromine. Its preparation is described by Kesting[76] as follows: The ethylene, prepared by conducting ethyl alcohol vapors over clay or aluminum oxide at 250° to 400° C., is passed into cold liquid bromine. The reaction, which is accelerated by sunlight, proceeds smoothly and the crude ethylene dibromide, after being washed with water, caustic soda, again with water, and dried with calcium chloride, is fractionated.[76a] About 95 per cent yields of ethylene dibromide are obtained.

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[70] Iiba and Nakatuka, Japanese Patent 91,487, 1931; assigned to Daiiti Kogyo Seiyaku K. K.; *Chem. Abs.*, 1932, **26**, 1703.

[71] De la Porte, French Patent 722,359, 1930; *Chem. Abs.*, 1932, **26**, 4195.

[72] *Ind. Eng. Chem.*, 1925, 17, 1182; *Chem. Abs.*, 1926, **20**, 359.

[73] Salzbergwerk Neu-Stassfurt and Theilnemher, German Patent 174,068, 1906; *Chem. Zent.*, 1906, **2**, 1297.

[74] Salzbergwerk Neu-Stassfurt and Theilnemher, British Patent 1,105, 1912; *J.S.C.I.*, 1912, **31**, 458. German Patent 248,982, 1912; *Chem. Zent.*, 1912, **2**, 299. Also Haberland and Schaefer, U. S. Patent 1,036,244, Aug. 20, 1912; assigned to Salzbergwerk Neu-Stassfurt and Theilnemher.

[75] E.g., Erlenmeyer and Bunte, *Ann.*, 1873, **168**, 64; *Chem. Soc. Abs.*, 1873, **26**, 1118. See also Kali-Forschungs-Anstalt G.m.b.H., British Patent 381,070, 1932; *Chem. Abs.*, 1933, **27**, 3952.

[76] *Z. angew. Chem.*, 1925, **38**, 362; *Chem. Abs.*, 1925, **19**, 2026.

The thermal combination of ethylene and bromine at glass surfaces has been studied very thoroughly by Williams.[77] The rate of reaction, under a variety of pressures, temperature and surface conditions, was determined by measuring the change in pressure of a mixture of ethylene and bromine vapor. Precautions were taken to exclude light as the reaction is slightly photosensitive.

At room temperature combination was found to be a surface reaction, which is in agreement with the results obtained by other investigators at 0° C. Furthermore the reaction appeared to be a simple addition of bromine to the double bond, unless the bromine was present initially in excess when an undetermined supplementary reaction took place.

The rate of reaction decreased with rise in temperature and the order of reaction was found to be either second, first, or zero (in one instance) depending on the glass surface. For a given glass surface, either lowering the temperature or increasing the pressure of the reactants lowered the order of the reaction. For a given glass surface and reaction order, the magnitude of the velocity coefficient was independent of the initial ethylene pressure; it did increase, however, with increasing initial bromine pressure.

The presence of water vapor was found to accelerate the reaction, while baking the glass containers before use removed this influence. A glass surface which exhibits a second order reaction when dry shows a first order reaction in the presence of water vapor. This seems to indicate that bromine is hydrated at the surface of the glass, and that the ethylene reacts with the bromine hydrate.

This transition from a second order to a first order reaction was observed also when the surface concentration of the bromine hydrate was so high that the chance of collision between a molecule of ethylene and a molecule of bromine hydrate was independent of the gaseous bromine pressure.

The rate of reaction was increased by the initial introduction of ethylene dibromide vapor and also there were some indications that reaction chains may start at the surface of the glass and then spread into the gas phase.

Williams[77a] showed that the reaction between ethylene and bromine in carbon tetrachloride was autocatalytic. Though Davis[77b] suggested that water may be a catalyst, this is not believed by Williams. Hydrobromic acid was found to increase the reaction velocity appreciably.

Ethylene dibromide may also be prepared by the catalytic combination of hydrogen bromide with either acetylene or vinyl bromide. According to Bauer,[78] the production of ethylene dibromide by the combination of two molecules of gaseous hydrogen bromide and acetylene proceeds quantitatively under the influence of strong sunlight or light from a quartz lamp; the same reaction can be carried out also in the vapor phase in the presence of oxidizing gases, such as air, oxygen, nitrogen peroxide, and ozone.[79] Reboul[80] made the remarkable discovery, to some extent substantiated by Wibaut, that when vinyl bromide is treated with very concentrated aqueous hydrobromic acid 1,2-dibromoethane is formed but with less concentrated acid 1,1-dibromoethane is formed. Wibaut[81] has shown that the direct combination of gaseous hydrogen bromide with vinyl bromide at 100° C. in the presence of glass wool and asbestos as catalysts produces mainly 1,2-dibromoethane; but silica gel and bismuth bromide and ferric bromide—if used without a support—direct the reaction to the formation of the 1,1-isomer. It was also shown that 1,2-dibromoethane can be obtained in reasonable yields from acetylene and gaseous hydrogen bromide in the presence of ferric bromide or mercuric bromide on asbestos at 100° C. The addition of hydrogen bromide to vinyl bromide in solutions of hydrobromic acid was found to lead to the formation of 1,1-dibromoethane exclusively when acid of specific gravity 1.60 was used, although with stronger acid (of specific gravity 1.86) a mixture of isomers containing about 35 per cent of the 1,2-isomer was formed. In glacial acetic acid solution, 1,1-dibromoethane was always the main product of the reaction.

[76a] Heath and Keller (U. S. Patent 1,921,157, Aug. 8, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, 27, 5086) purified ethylene dibromide by steam distillation and fractionation.

[77] *J.C.S.*, 1932, 1747, 1758.

[77a] *J.C.S.*, 1932, 2911.

[77b] *J.A.C.S.*, 1928, 50, 2769.

[78] Bauer, U. S. Patent 1.540.748, June 9, 1925; assigned to Röhm and Haas. Also German Patent 368,467, 1922, and French Patent 546,163.

[79] German Patent 394,194, 1929.

[80] *Ann.*, 1870, 155, 30.

[81] *Rec. trav. chim.*, 1931, 50, 313; *Chem. Abs.*, 1931, 25, 2684.

Ethylene dibromide is a colorless, sweet-smelling liquid of melting point 10.0° C., boiling point 131.6° C. at 760 mm., and d^{20}_{4} 2.1816. It burns only with difficulty.

Ethylene dibromide has been used considerably in the past for various organic syntheses but it will probably be replaced for this purpose by the cheaper dichloride. The greatest application of the compound nowadays is in a mixture with tetraethyl lead as an anti-knock agent in motor fuels.[82] The lead is eliminated from the engine, after the explosion, in the form of its dibromide, the bromine being derived from ethylene dibromide. It is reported[83] that about 300,000 pounds of ethylene dibromide per month were exported in 1930 from Germany to the United States for use in connection with the production of anti-knocking agents. This bromide is probably made from ethylene extracted from coke-oven gas.

It is interesting to note that ethylene dibromide and olefin dibromides generally may be quantitatively reduced to the parent olefin by the aid of the zinc-copper couple of Gladstone and Tribe.[83a] This process is useful in the preparation and purification of olefins and has also been employed with success in the quantitative examination of olefin mixtures.[84] In some instances hydrogen in the presence of colloidal palladium will remove halogens from olefin halides without saturating the unsaturated linkages.[85]

ETHYLENE DI-IODIDE

Only brief mention need be made of this substance as it has not yet been used industrially to any large extent. In the laboratory, however, it is often used in the synthesis of organic compounds.

The reaction between iodine and ethylene to yield ethylene di-iodide has long been known. Semenow[86] observed the formation of this iodide when ethylene was passed into a paste of iodine and absolute alcohol; Faraday[87] reported its formation from iodine and ethylene in the presence of sunlight, while Regnault[88] showed the reaction took place in the dark when the reactants were warmed.

[82] Calcott and Parmelee, U. S. Patents 1.835,140 and 1,835,141, Dec. 8, 1931; both assigned to E. I. duPont de Nemours and Co., Inc. Wilson, U. S. Patent 1,815,753, July 21, 1931; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1932, 492.

[83] *Chem. Trade J.*, 1930, **87**, 405.

[83a] *Proc. Roy. Soc.* (*London*), 1872, **20**, 218; *Chem. Soc. Abs.*, 1872, **25**, 461.

[84] Manning, King and Sinnatt, *Dept. Scientific & Industrial Research, Tech. Paper* **19**, 1928.

[85] Rosenmund and Zetzsche, *Ber.*, 1918, **51**, 578.

[86] *Jahresber.*, 1864, 483.

[87] *Annals of Philosophy*, 1820, **18**, 118; Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1853, **8**, 362.

[88] *Ann.*, 1835, **15**, 67.

The reaction between ethylene and iodine appears to differ from those between ethylene and chlorine or bromine since it is reversible under ordinary conditions, and at equilibrium appreciable quantities of both ethylene and iodine are found. This equilibrium has been investigated by Mooney and Ludlam,[89] who were interested in the reaction in the gaseous phase and over a temperature range of 11° to 65° C. The same reaction has been studied in carbon tetrachloride solutions at temperatures varying from 120° to 150° C. by Polissar.[90]

Mooney and Reid[91] have pointed out that at 30° C. combination between iodine and ethylene is a surface reaction taking place almost entirely on the surface of the solid iodine. Glass surfaces were found to be unimportant as catalysts, and the rate of the reaction was found to be proportional to the square of the pressure of the ethylene.

Ethylene also reacts with cyanogen iodide to yield ethylene di-iodide; analogous reactions do not take place between cyanogen chloride or bromide and this olefin. The reaction was considered to take place in two steps: first the dissociation of cyanogen iodide into cyanogen and iodine, followed by the reaction of the iodine formed with the ethylene. This can be represented by the following equations:

$$2CNI \rightleftharpoons (CN)_2 + I_2$$

$$C_2H_4 + I_2 \longrightarrow CH_2ICH_2I$$

Ethylene di-iodide is a crystalline solid, melting at 81°-82° C., and having a specific gravity of 2.07. It is soluble in alcohol, and only slightly soluble in water.

Propylene Dichloride (1,2-Dichloropropane)

As already indicated, the addition of halogens to propylene proceeds much more rapidly than in the case of ethylene. In the chlorination of propylene it is very difficult to prevent simultaneous substitution reactions which result in the formation of some higher chlorinated products. For example, Goudet and Schenker,[92] by passing an equimolecular mixture of propylene and chlorine slowly through a cooled illuminated tube, and immediately washing the product with sodium carbonate solution, obtained an 80 per cent yield of propylene dichloride, together with small amounts of 1,2,2-trichloro- and 1,1,2,2-tetrachloro-propanes.

Propylene dichloride may be prepared also by the action of liquid chlorine on gaseous or liquid propylene, particularly in the presence of an inert solvent such as carbon tetrachloride or of propylene dichloride itself. Using an excess of liquid propylene, the product is pure dichloride, but if an excess of chlorine is employed the dichloride is obtained mixed with trichloropropane, and other higher chlorinated propanes.[93]

Propylene dichloride is a colorless liquid of boiling point 96.8° C. at 760 mm., d^{14}_{4} 1.66, n^{20}_{D} 1.4388, and possessing chemical and physical properties very similar to those of ethylene dichloride. It has been prepared in comparatively large quantities and will probably find important applications in chemical industries, possibly as a solvent or as a raw material for chemical synthesis. For example, it may be condensed with ammonia to give a diamine; or with sodium cyanide to yield a dinitrile, hydrolyzable to a methylsuccinic acid; or the dichloride may be hydrolyzed with aqueous sodium carbonate to give propylene glycol. It has also been suggested for the dehydration of acetic and other aliphatic acids.[93a] On treatment with alcoholic potassium hydroxide it gives a mixture (yield 95 per cent) of two isomeric chloropropylenes.

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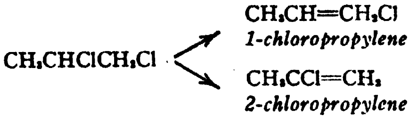
[89] *Proc. Roy. Soc. Edin.*, 1929, 49, 160.

[90] *J.A.C.S.*, 1930, 52, 956.

[91] *J.C.S.*, 1931, 2597.

[92] *Helv. Chim. Acta*, 1927, 10, 132; *Brit. Chem. Abs.* A, 1927, 440; *Chem. Abs.*, 1927, 21, 2657.

[93] Union Carbide Co.; British Patent 137,247, 1919; *Chem. Abs.*, 1920, 14, 1341. *Cf.* British Patent 136,489, 1919; *Chem. Abs.*, 1920, 14, 1122, for the preparation of ethylene dichloride. Also Curme, U. S. Patent 1,315,547, Sept. 9, 1919; assigned to Union Carbide Co.; *J.S.C.I.*, 1919, 38, 848A.



$$CH_3CHClCH_2Cl \; \begin{array}{l} \nearrow CH_3CH{=}CH_2Cl \\ \quad \textit{1-chloropropylene} \\ \searrow CH_3CCl{=}CH_2 \\ \quad \textit{2-chloropropylene} \end{array}$$

Fractional distillation of this mixture of isomers yields 25 to 30 per cent of the 2-isomer ($n^{6.5}_D$ 1.404) the remainder being a mixture of constant boiling point (boiling point 30° to 32° C.) consisting mainly of the 1-isomer.[94] Although the elimination of hydrogen chloride, either catalytically or under the influence of alkalies, from propylene dichloride does not normally yield allyl chloride, a mixture of chloropropylenes being usually obtained, the production of allyl chloride from propylene by passing this substance in the vapor state over a calcium chloride catalyst at 300° to 350° C. has been described by Essex and Ward.[95] Similarly allyl bromide is said to be formed from propylene dibromide, the reaction being represented as follows:

$$CH_3CHXCH_2X \longrightarrow CH_2{=}CHCH_2X + HX$$

$CH_3CHClCH_2Br$ was prepared by Friedel and Silva[96] by boiling propylene dibromide with mercuric chloride under a reflux apparatus. It is a limpid, colorless liquid of boiling point 120° C., d^0_4 1.585 and d^{16}_4 1.475, which has been used in chemical synthesis.

PROPYLENE DIBROMIDE (1,2-DIBROMOPROPANE)

This substance can be readily prepared by passing propylene into cooled bromine or bromine water.[97] It was obtained by Prunier[98] by passing the gaseous products of pyrolysis (at a "red" heat) of light petroleum oils, through a series of bottles containing bromine. Armstrong and Miller,[99] in their classical researches on the products of bromination of "oil gas", isolated propylene dibromide as well as ethylene dibromide and butadiene tetrabromide.

Propylene dibromide may also be obtained, often mixed with 1,3-dibromopropane, by the direct combination of hydrogen bromide and allyl bromide. The composition of the product depends to a large extent upon the conditions[100] but propylene dibromide is formed almost exclusively when allyl bromide is allowed to react with anhydrous hydrogen bromide in glacial acetic acid solution at 100°

[93a] Hartman, U. S. Patent 1,908,239, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3723; Canadian Patent 330,190, 1933; *Chem. Abs.*, 1933, **27**, 3224; U. S. Patent 1,908,240, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3723; all assigned to Eastman Kodak Co.; British Patent 383,148, 1932; assigned to Kodak, Ltd.; *Brit. Chem. Abs.* **B**, 1933, 139; Kodak-Pathé, French Patent 733,860, 1932; *Chem. Abs.*, 1933, **27**, 1007.

[94] Goudet and Schenker, *loc. cit.*

[95] U. S. Patent 1,477,047, Dec. 11, 1923; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1924, **18**, 537.

[96] *Bull. soc. chim.*, 1872, (2) **17**, 532.

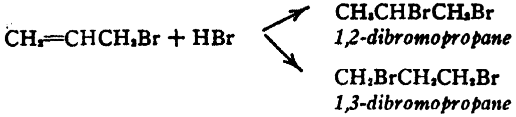
[97] Reynolds, *Ann.*, 1851, **77**, 120; Würtz, *Ann.*, 1857, **104**, 244; Gladstone and Tribe, *J.C.S.*, 1874, **27**, 409.

[98] *Bull. soc. chim.*, 1873, (2) **19**, 109.

[99] *J.C.S.*, 1886, **49**, 74. Schütz, Buschmann and Wissebach (*Ber.*, 1923, **56**, 869) also obtained the bromides of ethylene, propylene, butene-1, butene-2, pentene-1, and butadiene by brominating low temperature carbonization coal gas.

[100] Geromont, *Ann.*, 1871, **158**, 370; Reboul, *Ann. chim. phys.*, 1878, (5), **14**, 470; Erlenmeyer, *Ann.*, 1879, **197**, 169; Holleman and Matthes, *Verslag Akad. Wetens. Amsterdam*, 1918, **27**, 3.

C. in the dark or when allyl bromide is heated in the dark at 100° C. with only moderately concentrated hydrobromic acid.[101] The use of hydrobromic acid of specific gravity 1.650 leads mainly to the formation of the 1,2-dibromopropane (propylene dibromide) while more concentrated acid favors the production of the 1,3-isomer. The reactions may be written:



$$CH_2{=}CHCH_2Br + HBr \begin{cases} \nearrow CH_3CHBrCH_2Br \ \textit{1,2-dibromopropane} \\ \searrow CH_2BrCH_2CH_2Br \ \textit{1,3-dibromopropane} \end{cases}$$

Propylene dibromide is a colorless heavy liquid of boiling point 141.6° C. at 760 mm.,[102] melting point —55° C.[103] and d^{20}_{4} 1.9333.[102] So far as is known, it has never been produced on a large scale for industrial purposes. Its possible applications are as a solvent and raw material for organic synthesis.

On treatment with alcoholic potash, propylene dibromide gives rise to a mixture of two isomeric bromopropylenes and on continued treatment a mixture of methylacetylene and allene is produced.[104] Various halogenated propylenes have been described but they have not yet achieved industrial importance.[105]

It has been shown by Favorsky and Sokovnin[106] that propylene dibromide, when subjected to pyrolysis, undergoes transformation into its various isomers, probably by elimination and addition of hydrogen bromide.

It is interesting to note that propylene di-iodide may be prepared by treating allyl iodide, cooled to —18° C., with a current of dry hydrogen iodide,[107] the reaction being analogous to that of the bromide previously discussed.

THE DIHALIDES OF THE BUTENES

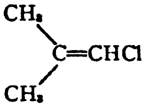
The action of chlorine on butene-1 and butene-2 leads to the production of the dichlorides of these two olefins in the normal way. The chlorination of a mixture of isomeric butenes, produced by the catalytic dehydration of n-butanol over alumina at 480° C. has been described by Briner, Hausser and de Luserna.[108] The reaction between chlorine and this butene mixture was inexplosive in character (the heat of reaction, $C_4H_8 + 2Cl \rightarrow C_4H_8Cl_2$ vapor, being 33.4 cal.); and the combination was best effected by a carefully regulated mixing of the reactants in a cooled tube. The properties of the dichlorobutane, so produced, were: boiling point 114.6°-114.8° C. at 760 mm.; freezing point, indefinite; n^{20}_{D} 1.4325; d^{0}_{4} 1.44; $d^{99.5}_{4}$ 1.032; flame point, 62° C. According to Briner and his collaborators, this dichlorobutane, in solvent power for oils and fats, is equal to carbon disulphide and ethylene dichloride.

The dihalides of butene-1 can exist in optically active forms while the dihalides of butene-2 contain two asymmetric carbon atoms in their molecule and are therefore capable of existing in four stereoisomeric forms, a *dl, d, l,* and *meso* (internally compensated). The *dl*-butene-1 dichloride boils at 124° C. and

[101] Wibaut, *Rec. trav. chim.*, 1931, **50**, 313.
[102] Kahlbaum, *Z. physik. Chem.*, 1898, **26**, 626, 646; *Chem. Soc. Abs.*, 1898, **74** (2), 556.
[103] Timmermans, *Bull. soc. chim. Belg.*, 1919, **28**, 392.
[104] Tapley and Giesy, *J. Amer. Pharm. Assoc.*, 1926, **15**, 115; *Chem. Abs.*, 1926, **20**, 3685.
[105] Friedel and Silva, *Compt. rend.*, 1872, **75**, 81; *Chem. Soc. Abs.*, 1872, **25**, 805; Markovnikov, *Ber.*, 1876, **8**, 1318; *Compt. rend.*, 1875, **81**, 668, 728, 776; *Chem. Soc. Abs.*, 1876, **29**, 338; Prins, German Patent 261,689, 1912; *Chem. Abs.*, 1913, **7**, 3641; Kirrmann and Grard, *Compt. rend.*, 1930, **190**, 876; *Chem. Abs.*, 1930, **24**, 3750.
[106] *Ann.*, 1907, **354**, 325, 358.
[107] Malbot, *Compt. rend.*, 1888, **107**, 113.
[108] *Helv. Chim. Acta*, 1924, **7**, 374; *Chem. Abs.*, 1924, **18**, 1977.

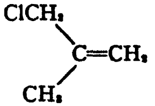
dl-butene-2 dichloride at 119° to 120° C.[109] On treatment with alkalies they both yield chlorobutenes.

The chlorination of isobutylene illustrates a rather general rule which was enunciated by Kondakoff[110] from a study of the chlorination of the amylenes, that olefins which combine very readily with mineral acids yield monochloro-olefins while those which do not readily combine with mineral acids give rise to the normal addition products on treatment with chlorine. In the case of isobutylene, Chechoukoff[111] found that treatment with chlorine resulted in the formation, not of the expected isobutylene dichloride, but of two isomeric chlorobutenes having the configurations:



$(CH_3)_2C{=}CHCl$

and



$(ClCH_2)(CH_3)C{=}CH_2$

The isobutylene dichloride, initially formed in this reaction, undergoes immediate decomposition with elimination of hydrogen chloride to yield chlorobutenes.

The bromine derivatives of the butylenes have been the subject of a number of important studies. Butene-1 dibromide, which is capable of optical activity, was prepared by Wurtz[112] by passing butene-1 into cooled bromine. It was similarly isolated by Lépingle,[113] together with other isomeric dibromides, by passing the gas produced by decomposing n-butanol (in the presence of alumina) into bromine. According to Lépingle it has the following physical properties: boiling point 166.3° C. at 760 mm., 50.8° C. at 13 mm. and d^{15}_4 1.8021. It solidifies at —65.4° C.[114] On treatment with alkalies it gives rise to a mixture of monobromobutenes[115] having the following formulas and physical properties:

(1) $CH_3CH_2CBr{=}CH_2$	b.p. 81.0° C. at 760 mm. m.p. —133.4° C. d^{15}_4 1.3209
(2) *cis*-$CH_3CH_2CH{=}CHBr$	b.p. 86.2° C. at 760 mm. d^{15}_4 1.3265
(3) *trans*-$CH_3CH_2CH{=}CHBr$	b.p. 94.7° C. at 760 mm. m.p. —100.3° C. d^{15}_4 1.3275

Butene-2 dibromide, existing in several stereoisomeric forms, was first produced by Wurtz.[116] Lépingle isolated two forms of this dibromide from the products of bromination of the gases resulting from the dehydration of n-butanol and assigned the following formulas to those compounds:

Meso-$CH_3CHBrCHBrCH_3$	b.p. 157.3° C. at 760 mm. b.p. 51.4° C. at 19 mm. m.p. —34.5° C. d^{16}_4 1.7913
dl-$CH_3CHBrCHBrCH_3$	b.p. 160.5° C. at 760 mm. b.p. 51–2° C. at 16 mm. d^{15}_4 1.7891

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[109] Timmermans, *Bull. soc. chim. Belg.*, 1919, **28**, 392.

[110] *Ber.*, 1891, **24**, 929.

[111] *Ber.*, 1883, **16**, 1869; *Bull. soc. chim.*, 1884, (2) **41**, 253; 1885, (2) **43**, 127.

[112] *Ann.*, 1869, **152**, 23.

[113] *Bull. soc. chim.*, 1926, **39**, 741; *Chem. Abs.*, 1926, **20**, 2974.

[114] Timmermans, *loc. cit.*

[115] Lépingle, *loc. cit.*

[116] *Ann.*, 1867, **144**, 236.

Later Young, Dillon and Lucas[117] obtained the stereoisomeric forms of butene-2 in a pure condition. On brominating the *cis*-isomer at 0° C., a dibromide of boiling point 75.6° to 75.8° C. at 50.0 mm., tentatively assumed to be the racemic compound, was obtained while the *trans*-hydrocarbon yielded a dibromide of boiling point 72.7° to 72.9° C. at 50 mm., which was probably the *meso*-isomer.

The halogenation of butane is said to be aided by simultaneously halogenating in the presence of 10 per cent by volume of butylene. The reaction is carried out in the dark at 0° to 30° C.[117a] On the other hand, when a mixture of butane and butylene is chlorinated in the presence of oxygen, the substitution reaction is stated to be suppressed.[117b]

On treatment with alcoholic potassium hydroxide, butene-2 dibromide was found by Hölz[118] to yield a monobromobutene, boiling point 87° to 88° C. at 760 mm., and having the structure $CH_3CBr{=}CHCH_3$. When this substance was treated with sodium ethoxide at 130° C. it was slowly converted into crotonylene, a further molecule of hydrogen bromide being eliminated. This reaction is typical of the olefin dihalides as a class.

Isobutylene dibromide, unlike the dichloride, may be obtained by the direct bromination of isobutylene.[119] However, some substitution also takes place and the isobutylene dibromide is always accompanied by higher brominated products. The approximate compositions by weight of the products of bromination of isobutylene at 45° to 50° C. and at 0° to 5° C. are given by Mereshkowsky[120] and by Hurd and Spence,[121] respectively, as follows:

	At 45° to 50° C. (Mereshkowsky)	At 0° to 5° C. (Hurd and Spence)
Isobutylene dibromide	45	65.5
Tribromoisobutane	44	25.5
Tetrabromoisobutanes	7	6.0
Penta- and hexa-bromoisobutane	1	3.0

Isobutylene dibromide is a colorless liquid, boiling point 150° C. at 760 mm.; melting point —70° C.; d^{20}_4 1.783; n^{15}_D 1.51406; n^{20}_D 1.51186.[122]

THE DIHALIDES OF THE AMYLENES

The chlorination of the various isomeric amylenes illustrates the rule of Kondakoff, already mentioned in the case of isobutylene, that the olefins which react very readily with mineral acids do not readily form the normal olefin dichlorides but tend to yield chloro-olefins instead. Thus Kondakoff[123] found that when pure trimethylethylene was treated with chlorine at 16° C. and —20° C., considerable quantities of hydrogen chloride were evolved and the products of chlorination consisted chiefly of chloroamylene and tertiary amyl chloride, with some amylene dichloride, the mechanism of formation of which may be summarized in the following manner:

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[117] *J.A.C.S.*, 1929, 51, 2528.

[117a] Bataafsche Petroleum Maatschappij, French Patent 745,543, 1933; *Chem. Abs.*, 1933, 27, 4240; see also Chapter 30.

[117b] Bataafsche Petroleum Maatschappij, French Patent 745,544, 1933; *Chem. Abs.*, 1933, 27, 4240.

[118] *Ann.*, 1889, 250, 230; *Chem. Soc. Abs.*, 1889, 56, 575.

[119] Linnemann, *Ann.*, 1872, 162, 36; Wurtz, *Ann.*, 1857, 104, 249; Hell and Rothberg, *Ber.*, 1889, 22, 1737.

[120] *Ann.*, 1923, 431, 113.

[121] *J.A.C.S.*, 1929, 51, 3561.

[122] Linnemann, *loc. cit.*; Krestinsky, *Ber.*, 1922, 55B, 2754; Timmermans, *loc. cit.*

[123] *J. Russ. Phys.-Chem. Soc.*, 1885, 17, 144 and 290; 1887, 19, 337; *Chem. Soc. Abs.*, 1885, 48, 736; 1886, 50, 136; 1888, 54, 123.

$C_5H_{10} + Cl_2 \longrightarrow C_5H_{10}Cl_2$ (*amylene dichloride*)

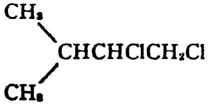
$C_5H_{10}Cl_2 - HCl \longrightarrow C_5H_9Cl$ (*chloroamylene*)

$C_5H_{10} + HCl \longrightarrow C_5H_{11}Cl$ (*tertiary amyl chloride*)

It was observed that the evolution of hydrogen chloride commenced only after a certain amount of chlorine had been absorbed, but once started this production of hydrogen chloride continued until the end of the operation. Besides the products enumerated above, others of higher boiling point (and consisting of $C_5H_{10}Cl$, $C_5H_9Cl_3$, $C_5H_8Cl_4$, with traces of C_5H_9Cl and $C_5H_{11}Cl$) are obtained if excess of chlorine is used or if the trimethylethylene is cooled with calcium chloride and snow.

When symmetrical methylethylethylene was treated with chlorine the chief product was the dichloride, $CH_3CHClCHClCH_2CH_2$, but a small quantity of the monochloropentene, $CH_3CHClCH{=}CHCH_3$ was also formed.[124]

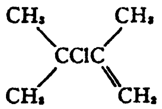
On the other hand, Kondakoff [125] found that isopropylethylene, which is also known to be less reactive toward mineral acids than methylethylethylene, gave the dichloride almost exclusively. Chlorine was passed into isopropylethylene maintained at temperatures from —20° C. to 16° C. but in all cases the products were the same, i.e., mainly isopropylethylene dichloride,



$$(CH_3)_2CHCHClCH_2Cl$$

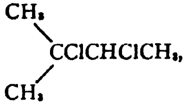
together with only a small amount of a monochloride.

It is interesting to note that tetramethylethylene, one of the more reactive of the isomeric hexenes, on treatment with chlorine at ordinary temperature, yields mainly a chlorotetramethylethylene,[126] probably



$$(CH_3)_2CClC{=}(CH_3)_2$$

Trimethylethylene Dichloride



Trimethylethylene dichloride, $(CH_3)_2CClCHClCH_3$, is a heavy oil, boiling point 133° to 135° C. at 760 mm.

According to the Badische Co.,[127] amylenes and hexenes readily yield dichlorides on treatment with sulphuryl chloride at temperatures below 30° C. The preparation of trimethylethylene dichloride can be conducted as follows: Sulphuryl chloride is gradually introduced with continuous stirring into an excess of trimethylethylene at —2° to 0° C. After a further period of agitation the sulphur dioxide and excess amylene are distilled off and the residue fractionated under reduced pressure. A good yield of trimethylethylene dichloride, boiling point 48° to 52° C. at 40 mm., is obtained.

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[124] Kondakoff, *Ber.*, 1891, **24**, 929; *Chem. Soc. Abs.*, 1891, **60**, 809.

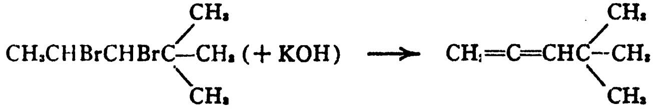
[125] *J. Russ. Phys.-Chem. Soc.*, 1888, **20**, 141; *Chem. Soc. Abs.*, 1889, **56**, 113.

[126] Choupotsky and Mariutza, *J. Russ. Phys.-Chem. Soc.*, 1890, **21**, 431; *Chem. Soc. Abs.*, 1890, **58**, 727.

[127] French Patent 433,309, 1911; *J.S.C.I.*, 1912, **31**, 151.

Isopropylethylene dichloride boils at 143° to 144.5° C. at 760 mm. and has d_4^0 1.1106, while symmetrical methylethylethylene dichloride has boiling point 138° to 139.5° C. at 760 mm.

Most of the industrial work so far reported on the chlorination of pentenes has as its primary object the production of monochloro compounds from which the monohydric alcohols can be obtained by hydrolysis. This is particularly so in the case of the amylenes and pentanes, as pointed out in Chapters 29 and 33. As indicated above the dihalides are substances of quite remarkable chemical activity which might be used for the synthesis of numerous new organic compounds. The higher homologues of allene may be synthesized from some of the olefin dihalides by treatment with caustic alkalies. In this way Favorskii[128] was able to prepare tertiary butylallene in 90 per cent yield by treating the dibromide of symmetrical methyl tertiary butylethylene with excess of caustic potash, the reaction proceeding according to the scheme:



$$CH_3CHBrCHBrC(CH_3)_3\ (+\ KOH) \longrightarrow CH_2{=}C{=}CHC(CH_3)_3$$

Higher Olefin Dihalides

The general properties of the higher olefin dihalides[129] are similar to those of the dihalides just described (such as those of tetramethylethylene and methylethylethylene). As yet they have not been employed industrially though they have been utilized in the chemical synthesis of organic substances.

A number of processes have been proposed for producing chlorinated hydrocarbons, or mixtures of such substances, by the interaction of chlorine with cracking gas or cracked gasoline. Thus, for example, Ellis and Wells[130] produced halogenated hydrocarbons by subjecting "acid extract" to the action of a halogenating agent. The term "acid extract" is here applied to an alkylsulphuric acid liquor obtained by absorption of olefins, from cracking operations, in sulphuric acid. Payne and Montgomery[131] suggest chlorinating the gaseous products of pressure distillation (i.e., cracking gas) in the presence of a catalyst made by treating a high-boiling paraffin oil with chlorine at 300° F. until a porous solid, having the appearance of coal, is obtained. In the presence of this porous catalyst chlorination is effected at about 300° F. and the most satisfactory yield of liquid chlorinated products is said to be obtained when using three volumes of chlorine per volume of gas. The process of Payne and Montgomery evidently includes not only the chlorination of the olefins present in the gas but also the substitutive chlorination of saturated hydrocarbons.

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[128] *J. Russ. Phys.-Chem. Soc.*, 1920, 50, 557; *Chem. Abs.*, 1924, 18, 1466.

[129] For the dibromides of the higher olefins see Kirrmann, *Bull. soc. chim.*, 1926, 39, 988; 3-methyl-3-pentene dibromide is described by Pariselle and Simon, *Compt. rend.*, 1921, 173, 86; for hexene dibromides see Timmermans, *Bull. soc. chim. Belg.*, 1919, 28, 392.

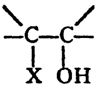
[130] U. S. Patent 1,440,976, Jan. 2, 1923; *J.S.C.I.*, 1923, 42, 202A.

[131] U. S. Patent 1,520,506, Dec. 23, 1924; *J.S.C.I.*, 1925, 189B. U. S. Patent 1,453,766, May 1, 1923; *J.S.C.I.*, 1923, 42, 801A. Both patents assigned to Standard Oil Co. of Indiana.

Chapter 21

Production, Properties and Uses of Halohydrins Derived from Simple Olefins

The halohydrins are compounds containing in their molecule both a halogen atom and a hydroxyl group, or in other words, are halogenated alcohols. The halohydrins derived from the simple monolefins belong exclusively to the class of 1,2- (or α) derivatives, in which the halogen atom and hydroxyl group are linked to adjacent carbon atoms and possess the following general structure:



where X represents a halogen atom. From an industrial point of view only the α-chlorohydrins exemplified by the simplest member, ethylene chlorohydrin, are of importance though the corresponding bromohydrins and iodohydrins are also known. Halohydrins in which the halogen atom and hydroxyl group are not attached to continuous carbon atoms also exist, but as they cannot be produced directly from olefins and are of little industrial interest they are not considered in the following account.

Numerous methods are available for the synthesis of the α-halohydrins, but most of them are of academic interest only. The interaction of the simple monolefins with hypochlorous acid, or chlorine water, is the only method of technical significance.

Although ethylene chlorohydrin was discovered as early as 1859 by Wurtz,[1] and its remarkable chemical reactivity clearly demonstrated, this substance continued to possess merely an academic importance until the beginning of the present century when attempts were made to use it in the synthesis of indigo. During the World War it assumed a great importance in Germany as an intermediate in the manufacture of mustard gas, but it was not until afterwards that ethylene chlorohydrin was used in comparatively large amounts for the preparation of other chemical materials. The most important factors which have contributed to a revival of interest in the olefin chlorohydrins are: first, the increasing production of large amounts of the lower olefins in commercial cracking operations (and especially in vapor-phase high-temperature cracking) and, second, the continued growth of the liquid chlorine industry with its economy of production and perfection of methods of bulk transport. Although most of the actual chemistry of the chlorohydrins has been known for half a century, changed manufacturing conditions and the development of the oil-cracking industry have combined to direct attention to the synthetic possibilities of the 1,2-chlorohydrins.

The importance of the α-chlorohydrins is due entirely to the extraordinary reactivity of the chlorine atom in these compounds, which renders possible the synthesis of a large number of organic substances, for example, solvents and drugs, from these halogenated alcohols. Possibly the greatest application of α-chlorohydrins is in the manufacture of glycols, olefin oxides, and their derivatives, which may be utilized as solvents or fumigants. In brief, the chlorohydrins derived from the simple monolefins are to be regarded as chemical intermediates in industrial syntheses possessing great potentialities.

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[1] *Ann.*, 1859, 110, 125; prepared by the action of hydrogen chloride on glycol. Carius (*Ann.*, 1863, 126, 197) used ethylene and hypochlorous acid.

The reactions of ethylene chlorohydrin are a good example of the α-halohydrins as a class. Attention should be drawn to the reactivity of the halogen atom in the halohydrins as compared with the halogen atoms in the olefin dihalides. Whereas ethylene dichloride reacts only slowly in sodium carbonate solution at 100° C., ethylene chlorohydrin is hydrolyzed by water alone (about 15 per cent at 97° C. in 12 hours) and is quantitatively converted into ethylene glycol in one hour by sodium carbonate solution at 105° C.[2] Many other illustrations might be advanced. For example, ethylene chlorohydrin reacts with sodium sulphide to yield a thiodiglycol, with amines or caustic alkalies to form ethylene oxide, and with alkali cyanides to give the corresponding nitrile. Further, the reactivity of the chlorine atom is not greatly affected by esterifying the hydroxyl group and esters of the glycols may be prepared by the action of the sodium salts of organic acids on the chlorohydrin.

ETHYLENE CHLOROHYDRIN (α-CHLOROETHYL ALCOHOL, CH_2ClCH_2OH)

The earlier methods of preparation consisted in passing dry hydrogen chloride gas through ethylene glycol at about 150° C., the chlorohydrin distilling over as formed.[3] This rather troublesome method has been entirely superseded by the direct combination of hypochlorous acid with ethylene, a reaction discovered by Carius.[4] The earlier workers were apparently misled by the idea that fairly strong solutions of hypochlorous acid were necessary. It has since been demonstrated that the formation of chlorohydrins proceeds smoothly when olefins are passed into dilute aqueous solutions of hypochlorous acid at atmospheric temperature. Conditions which promote the solution of the gas in the aqueous solution (e.g., agitation or increased pressures) accelerate the formation of chlorohydrin.[5]

Formerly, hypochlorous acid was made by the action of chlorine water on mercuric oxide, or through the medium of chlorine oxide.[6] Lauch[7] and Bamberger[8] added a weak acid, such as boric acid, to a dilute aqueous solution of a hypochlorite. A better method is that of Wohl and Schweitzer,[9] which consists in passing chlorine into a cooled solution of sodium carbonate or bicarbonate. A variation of the latter is the adding of an excess of sodium bicarbonate to an alkaline solution of sodium hypochlorite.[10]

Before the World War the Badische Anilin- und Soda-Fabrik worked on the production of ethylene chlorohydrin with the object of synthesizing indigo, the source of hypochlorous acid being calcium hypochlorite.[11] The method for large scale preparation of ethylene chlorohydrin, developed in Germany during the World War, consisted essentially in the liberation of hypochlorous acid from bleaching powder by gaseous carbon dioxide in the presence of ethylene gas. This process has been described by Norris[12] as follows:

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[2] Brooks, *Chem. Met. Eng.*, 1920, **22**, 631.

[3] Ladenburg, *Ber.*, 1883, **16**, 1408. Wurtz, *Ann.*, 1859, **110**, 125.

[4] *Ann.*, 1863, **126**, 197; Butlerow, *Ann.*, 1866, **144**, 40.

[5] Brooks, *Chem. Met. Eng.*, 1920, **22**, 631.

[6] Reformatsky, *J. pr. Chem.*, 1889, **40**, 396.

[7] *Ber.*, 1885, **18**, 2287.

[8] *Ann.*, 1895, **288**, 81.

[9] *Ber.*, 1907, **40**, 94.

[10] Walker, U. S. Patents 972,952, Oct. 11, 1910, and 972,954, Oct. 18, 1910; assigned to Maas and Waldstein Co.; *Chem. Abs.*, 1911, **5**, 150, 160.

[11] German Patent 163,043, 1904; *Chem. Zentr.*, 1905, **2**, 1062.

> The reaction was carried out in a cylindrical tank resting on its side, furnished with stirrers and well insulated. Enough chloride of lime was introduced to furnish 500 kilograms of available chlorine, together with 5 cubic meters of water. At first about 20 cubic meters of carbon dioxide alone were passed in and later, carbon dioxide and ethylene simultaneously. The reaction should be carried out at as low a temperature as possible and in practice the temperature could be maintained at 5° to 10° C. by continuously pumping the liquid through a coil cooled by brine. The rate of absorption of the ethylene was carefully noted and more carbon dioxide was introduced as soon as ethylene absorption slackened. When ethylene was no longer absorbed, i.e., in about 2 to 3 hours, the contents of the apparatus were filtered to remove calcium carbonate whereupon the residual liquor, containing 10 to 12 per cent of chlorohydrin, was distilled with steam to yield a condensate containing 18 to 20 per cent of chlorohydrin. The yield of chlorohydrin calculated on the ethylene used was 60 to 80 per cent of the theoretical.

According to Brooks,[13] the gradual liberation of hypochlorous acid from sodium hypochlorite in the presence of ethylene or propylene by weak acids (boric acid or carbon dioxide) gives yields of only 25 to 30 per cent based on the original quantity of hypochlorite. Somewhat better results are obtainable by using bleaching powder and carbon dioxide. This is probably due to the case of decomposition of sodium hypochlorite solutions the instant free hypochlorous acid is formed by the neutralization of the excess alkali. In the presence of excess free alkali, concentrated sodium hypochlorite solutions are quite stable.[14]

The principal methods which have been preposed for obtaining aqueous solutions of hypochlorous acid are as follows: passage of carbon dioxide into aqueous solutions of calcium or sodium hypochlorite; passage of chlorine into sodium carbonate solutions; introduction of chlorine and caustic alkali simultaneously; introduction of aqueous sodium bicarbonate into aqueous sodium hypochlorite. Other procedures are the introduction of chlorine into water either alone or in the presence of certain metallic salts, e.g., copper chloride or oxychloride,[15] or salts such as disodium hydrogen phosphate capable of neutralizing the hydrogen chloride simultaneously formed.[16]

The important fact that ethylene chlorohydrin may be produced by passing chlorine and ethylene simultaneously into water was established by Gomberg.[17] Previously, Read and Williams[18] had shown an analogous reaction takes place between bromine water and ethylene. Although it is well known that in the system,

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

the proportions of hypochlorous and hydrochloric acids actually present under normal conditions are very small, the velocity of the reaction between the hypochlorous acid and ethylene is so much greater than that between free chlorine and ethylene that it was possible to obtain good yields of chlorohydrin and to suppress the competitive reaction of direct chlorination. According to Gomberg, when ethylene and chlorine are passed into water, keeping the ethylene in slight excess, a concentration of chlorohydrin of 6 to 8 per cent is reached before an appreciable amount of dichloride is formed. Up to this point the gases are absorbed rapidly at 10° to 12° C., but thereafter the reaction becomes sluggish. The influence of dissolved chlorohydrin, hydrogen chloride or metallic chlorides on the course of the reaction was roughly determined. Chlorohydrin itself is rather helpful at the beginning, and hydrochloric acid up to concentrations of 2 moles per liter does not hinder the almost exclusive formation of chlorohydrin. The combined effect is, however, more important since, when both are present in concentrations of 1 mole per liter production of dichloride is favored. Any attempt to shift the equilibrium $H_2O + Cl_2 \rightleftharpoons HOCl + HCl$ by removing the hydrochloric acid from the sphere of the reaction by the addition of metallic salts is not beneficial as these promote dichloride formation. Efficient stirring is necessary for good yields. Gomberg considered more than 8 per cent concentration of ethylene chlorohydrin in the reaction mixture inadvisable.

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[12] *Ind. Eng. Chem.*, 1919, 11, 817.

[13] *Chem. Met. Eng.*, 1920, 22, 631.

[14] Muspratt and Smith, *J.S.C.I.*, 1898, 17, 1096; 1899, 18, 210.

[15] Kerfoot, Kerfoot, Irvine and Haworth, British Patent 128,635, 1917; *J.S.C.I.*, 1919, 38, 657A; U. S. Patent 1,227,049, May 22, 1917; *J.S.C.I.*, 1917, 36, 712; British Patent 12,912, 1915; *J.S.C.I.*, 1916, 35, 1059.

[16] Eldred and Brooks, U. S. Patent 1,465,601, Aug. 21, 1923; *Chem. Abs.*, 1923, 17, 3880.

[17] *J.A.C.S.*, 1919, 41, 1414.

[18] *J.C.S.*, 1917, 111, 240.

An interesting extension of Gomberg's method for the preparation of chlorohydrins is described by Ernst,[19] who effects the synthesis of chlorohydrin-ethers by causing a mixture of an olefin and chlorine to react with an alcohol, with or without the addition of water. Thus, ethylene and chlorine are passed into ethanol to furnish an 85 per cent yield of β-chloroethyl ether, $C_2H_5OCH_2CH_2Cl$.

Brooks[20] has given some details of the operation of a plant for the production of ethylene and propylene chlorohydrins by the use of chlorine water. The apparatus was of the liquid-circulating type. To minimize the corrosion difficulties the free hydrochloric acid was neutralized with soda ash. It was shown that the formation of chlorohydrins was fairly rapid until the solution contained about 5 per cent of chlorohydrins. According to Curme,[21] temperature has only a slight influence on the yield of ethylene chlorohydrin by this process and a little dichloride is always formed as a by-product.

An examination of the synthesis of ethylene chlorohydrin from hypochlorous acid and ethylene was made by Bozza and Mamoli.[22] They observed that the direct attack of ethylene by chlorine and also the action of chlorine on chlorohydrin became appreciable only when the concentration of the latter was about 1 molar. In the presence of solutions of pure hypochlorous acid the velocity of the chlorohydrin-forming reaction was independent of the concentration of the acid within wide limits but did depend upon the surface area of the ethylene bubbles. The velocity of this reaction is not altered by adding benzene or carbon tetrachloride or by starting with solutions already acid. It is diminished by the presence of sodium chloride, so that it is disadvantageous to neutralize the acid with alkali. The presence of copper salts induces considerable formation of secondary products while neutralization with lead oxide is valueless. The action of chlorine on chlorohydrin solutions of medium concentration yields highly chlorinated products very difficult to separate by distillation. Bozza and Mamoli concluded that, to avoid losses due to secondary reactions, the practical limit of chlorohydrin concentration was 8 to 10 per cent.

Shilov[23] recorded some experiments directed toward the development of an industrial method of manufacturing ethylene chlorohydrin. Hypochlorous acid was made by adding alkali or alkaline hypochlorite to a solution of chlorine in water rather than by passing chlorine into an alkaline solution. This operation was effected by first passing chlorine into a flask cooled by ice and containing a little water; after the formation of a chlorine hydrate precipitate, a solution of sodium hydroxide, or better, of sodium hypochlorite, was added (with good stirring) at such a rate that chlorine always remained in excess. When the reaction was completed, excess chlorine was removed by air-blowing or by adding a small quantity of calcium carbonate. By this method about 5.25 per cent solutions of hypochlorous acid, sufficiently stable for the chlorohydrin synthesis, were prepared. The reactions taking place were considered to be

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[19] German Patent 537,696, 1928; assigned to Alexander Wacker Ges. für Elektrochemische Ind. G.m.b.H.; *Chem. Abs.*, 1932, **26**, 1297.

[20] *Chem. Met. Eng.*, 1920, **22**, 631. U. S. Patent 1,446,874, Feb. 27, 1923; assigned to Chadeloid Chemical Co.; *J.S.C.I.*, 1923, **42**, 377A.

[21] *Chem. Met. Eng.*, 1921, **25**, 999.

[22] *Giorn. Chim. Ind. Appl.*, 1930, **12**, 283; *Brit. Chem. Abs.*, **A**, 1930, 1269.

[23] *J. Chem. Ind. (Moscow)*, 1928, **5**, 1273; *Chem. Abs.*, 1929, **23**, 2937.

$$Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$$
$$Cl_2 + NaOCl + H_2O \longrightarrow 2HOCl + NaCl$$

Experiments indicated that the velocity of ethylene absorption in hypochlorous acid increased with the rate of stirring, and the formation of chlorohydrin was catalyzed by hydrogen ions. When the hydrogen-ion concentration (and consequently the hypochlorous acid concentration) drops below the neutral reaction point, ethylene absorption becomes very slow. The yield of chlorohydrin, calculated from the hypochlorous acid present, was 80 per cent when using dilute solutions. It was found also that the chlorohydrin is only slightly oxidized by the free hypochlorous acid.

Conditions for the preparation of ethylene chlorohydrin by the action of chlorine and water on ethylene have been investigated by Zapadinskii.[24] He carried out this reaction in the following manner: Chlorine and ethylene are passed simultaneously (through tubes terminating in narrow outlets) into the bottom of a 1.5 liter flask containing 500 cc. of water, maintained at ±2° C. and vigorously stirred. The pressure was 150 to 200 mm. of water. Experiments with ethylene dichloride (to increase the solubility of chlorine) and with alcohol (to increase the solubility of ethylene) resulted in considerably decreased yields since the ethylene dichloride suppresses the hydrolysis of the chlorine, and the alcohol undergoes oxidation at the expense of the chlorine. Brooks' suggestion to employ gasoline as a solvent is considered by Zapadinskii to be of doubtful value. In order to separate the chlorohydrin produced, three operations are proposed. The reaction mixture is distilled, and the first 10 to 12 per cent of distillate contains 80 to 85 per cent of the chlorohydrin; the next 10 to 15 per cent contains most of the remainder and only 2 to 3 per cent is found in the residue. The second distillate fraction is added to fresh crude material while the first distillate is extracted with ethylene dichloride, which is itself a by-product of the process. It is advisable to extract twice with this dichloride, containing some chlorohydrin, then twice with pure dichloride, taking each time a volume of solvent equal to 20 per cent of the solution. The third and final operation consists in separating the chlorohydrin from the dichloride by distillation, either at ordinary or reduced pressures.

The synthesis of ethylene chlorohydrin by Gomberg's method has been systematically studied by Tropsch and Kassler.[25] Their results are in substantial agreement with those of other investigators. Measured volumes of ethylene and chlorine were conducted into a water-filled bottle, mechanically shaken, and analyses were made of the gases escaping at the outlet. The occurrence of the two competitive reactions yielding ethylene chlorohydrin and ethylene dichloride, respectively, was noted and the influence of various factors on the relative yields of these two products investigated. Conditions found to favor the production of ethylene chlorohydrin were (1) the use of excess ethylene in the entering gases, and (2) the maintenance of a low concentration of ethylene chlorohydrin in the reaction mixture. On the other hand, the yield of ethylene dichloride rose linearly with increasing concentration of ethylene chlorohydrin.

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[24] *J. Chem. Ind. (Moscow)*, 1928, 5, 1426; *Chem. Abs.*, 1929, 23, 3208.

[25] *Mitt. Kohlenforschungsinst. Prag.*, 1931, No. 1, 16; *Chem. Abs.*, 1932, 26, 1242; French Patent 732,106, 1932; *Chem. Abs.*, 1933, 27, 732; also British Patent 377,595, 1932; *Brit. Chem. Abs.* B, 1932, 973.

The following empirical formula was developed to express the relationship between the ratio, *y*, of the extent to which the competitive reactions, yielding chlorohydrin and dichloride respectively, proceed at a chlorohydrin concentration, *x*, and at definite partial pressures of chlorine and ethylene:

$$y = -1.312x + 0.182P + 8.66,$$

$$\text{where}\quad P = \frac{100\,p_{C_2H_4}}{p_{C_2H_4} + p_{Cl_2}},\ \text{and}$$

$p_{C_2H_4}$ and p_{Cl_2} are the partial pressures of ethylene and chlorine, respectively. Thus, in an experiment at 20° C., the reaction producing ethylene dichloride occurred to the extent of 20 per cent (based on the ethylene reacting) when the concentration of ethylene chlorohydrin was 7 per cent. For economical production of ethylene chlorohydrin, therefore, a limited concentration of it in the reaction mixture should be maintained by continuous dilution. The introduction of ethylene dichloride into the reaction mixture increased the formation of dichloride, probably by solution and direct combination of ethylene and chlorine in the oily phase. In agreement with other investigators, Tropsch and Kassler observed that the reaction rate of hypochlorous acid and ethylene was very rapid up to 10 per cent concentration. Temperature variations from 4° C. to 30° C. had little influence on the reaction, but the yield of dichloride at 40° to 60° C. was distinctly reduced.

According to Frahm,[26] the rate of formation of ethylene chlorohydrin is increased, and that of the dichloride diminished, if ethylene and chlorine are allowed to react in dilute aqueous solutions of various catalysts, e.g., in 0.1 to 1.0 per cent copper chloride or ferric chloride solutions. Since these substances facilitate the decomposition of hypochlorous acid into hydrochloric acid and oxygen, Frahm suggested that ethylene and chlorine in aqueous media give ethylene oxide, which subsequently reacts with hydrogen chloride.

TECHNICAL PRODUCTION OF CHLOROHYDRINS

The majority of the methods dealing with the manufacture of chlorohydrins refer to the treatment of cracking gas or oil gas as a source of olefinic hydrocarbons. The products, therefore, consist not only of ethylene but also of propylene chlorohydrin and possibly chlorohydrins of the immediately higher homologues of propylene. For this reason the procedures are discussed as a whole.

Walker[27] prepared chlorohydrins of the higher olefins (boiling point 35° to 125° C.) containing 5 to 8 carbon atoms per molecule by the following method. Hypochlorous acid is made by adding sodium bicarbonate (75 parts of $NaHCO_3$ to 75 parts of NaOCl) either in solid form or in aqueous solution to an aqueous 15 to 25 per cent solution of sodium hypochlorite. The hypochlorite solution is then added to the olefinic hydrocarbon with agitation and cooling. The reac-

[26] *Rec. trav. chim.*, 1931, 50, 261; *Brit. Chem. Abs.* A, 1931, 598.
[27] U. S. Patents 972,952 and 972,953, Oct. 18, 1910.

tion should continue for about four hours at a temperature of 15° C. or below. The mixture separates into two layers, an aqueous layer which is withdrawn and an oily layer (consisting of chlorohydrins and hydrocarbons). The latter is washed with water, dehydrated, and the chlorohydrins (boiling point about 170° C.) separated from lower-boiling hydrocarbons by distillation.

Kerfoot and his co-workers[28] prepared chlorohydrins, particularly ethylene chlorohydrin, by alternately passing chlorine and ethylene into an aqueous solution of a copper salt, either chloride or oxychloride. The mixture is vigorously agitated to secure good contact. A modification consists in allowing the aqueous solution to flow down a packed tower divided into a number of horizontal zones alternately filled with chlorine and ethylene. The chlorohydrins are separated from the aqueous solution by extraction with ether, or in the case of ethylene chlorohydrin, a constant-boiling mixture (43 per cent chlorohydrin and 57 per cent water, boiling point 97° C.) is obtained by fractional distillation.

McElroy[29] described the production of chlorohydrins by interaction of olefins (either pure individuals or mixtures) with aqueous solutions of chlorine or hypochlorous acid, generated electrolytically. Olefin dichlorides are formed simultaneously and it is largely a question of the relative concentrations of the chlorine, water, and olefin which determines the course of the reaction. In the presence of a large excess of water the chlorohydrin-forming reaction predominates. The aqueous bath is saturated with an excess of olefin by agitation, this being advantageous since it increases the rate of formation of chlorohydrin and also shields the latter substance from further chlorination.

It is also proposed to make chlorohydrins by allowing olefin gases to react with chlorine in the presence of excess steam and water at a temperature of about 100° C.[30] The following conditions appear to be necessary: (1) The concentrations of steam and ethylene should always be very much greater than that of the chlorine; (2) olefin dichlorides are formed unless steam is in considerable excess; (3) chlorine should always be in relatively low concentrations; (4) the reaction develops much heat which is absorbed by the steam; (5) the continued condensation (and evaporation) of water carries the hydrogen chloride formed into the liquid phase so that it may be continuously removed from the reaction zone.

McElroy[31] suggested carrying out the same reaction in a tower at the bottom of which the mixed olefin gases are introduced. The gases pass upwards against a downflowing current of hot water which furnishes the water vapor necessary for dilution and reaction and also serves as a scrubbing means to remove hydrogen chloride. Chlorine is added at various points in the tower and the temperature is so maintained that the desired products together with water vapor pass from the top of the tower and are condensed. Hydrochloric acid is removed continuously at the bottom.

In connection with these processes of McElroy, Brooks[32] has recorded that large-scale operation leads to the formation of large proportions of highly chlorinated oily products.

Another process for making chlorohydrins depends essentially on the employment of metallic chlorides, such as cupric or ferric chlorides, for supplying the chlorine.[33] The reduced chloride (cuprous or ferrous chlorides) is then reconverted into the initial materials by oxidation with air followed by treatment with hydrochloric acid. Thus, a mixture of olefins and steam is conducted over cupric chloride (or ferric chloride) suspended on a carrier, at temperatures of over 100° C., best at about 160° C.

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[28] British Patent 128,635, 1917; *J.S.C.I.*, 1919, **38**, 657A.

[29] U. S. Patent 1,253,615, Jan. 15, 1918; *Chem. Abs.*, 1918, **12**, 702.

[30] McElroy, U. S. Patent 1,253,616, Jan. 15, 1918; *Chem. Abs.*, 1918, **12**, 703.

[31] U. S. Patent 1,295,339, Feb. 25, 1919; *Chem. Abs.*, 1919, **13**, 1217.

[32] *Chem. Met. Eng.*, 1920, **22**, 631.

[33] McElroy, U. S. Patent 1,315,229, Sept. 9, 1919; *Chem. Abs.*, 1919, **13**, 2880.

The process of Moness[34] consists in passing a mixture of gaseous olefins (cracking gas), chlorine, and steam, into a reaction chamber at 97° to 100° C. packed with materials, such as manganese dioxide, which are capable of reacting with the hydrochloric acid produced to yield more chlorine. Various other substances may be employed to combine with the hydrochloric acid, e.g., magnesium oxide or zinc oxide, or oxidizing compounds such as chromates or ferric oxide. The products consist of an aqueous solution of chlorohydrins together with a separate oily layer containing olefin dichlorides.

Brooks[35] described a treatment of ethylene or cracking gas which consists in passing these olefins, under 5 to 10 atmospheres pressure, into chlorine water at 10° to 20° C., with violent agitation and in the presence of an immiscible solvent for chlorohydrins, e.g., chloroform, carbon tetrachloride, tetrachloroethane, dichloroethane, benzol, and toluol. The presence of the immiscible solvent tends to remove the chlorohydrin from the aqueous solution and thus prevents its being further acted upon by chlorine.

In another procedure,[36] unsaturated hydrocarbons are mixed with an aqueous solution of an alkali carbonate or bicarbonate, and chlorine is then introduced into the aqueous (i.e., bottom) layer. Reaction between the dilute hypochlorous acid solution and the unsaturated hydrocarbons is facilitated by vigorous agitation or by circulating or atomizing one liquid through the other. The maximum strength of hypochlorous acid is about 3 per cent. The chlorohydrins produced are said to be substantially free from dichlorides.

As a method of isolating chlorohydrins, Brooks[37] suggested adding a neutral salt (sodium or magnesium chloride or sulphate) to the aqueous solution, separating the oily layer which forms, and then extracting the latter with a solvent immiscible with water, such as benzol or carbon tetrachloride. The use of benzol as a dehydrating agent has been suggested also by Kirst.[38]

In the process of Eldred,[39] chlorohydrins are obtained by adding successive portions of chlorine and olefin-containing gases, such as oil gas, to a flowing stream of steam, while permitting time for reactions between successive additions.

Curme and Young[40] employ a solution of a hypochlorite containing free hypochlorous acid, and Eldred and Brooks[41] use solutions of an alkali salt of a weak acid (e.g., sodium carbonate, bicarbonate, borate or phosphate) which has previously been treated with chlorine and therefore contains free hypochlorous acid.

The following procedure was described by Long, Willson and Wheeler.[42] Water is circulated through a number of reaction vessels, in some of which it is treated with halogen while in others (alternately spaced) the halogenated liquid, containing free hydrochloric and hypochlorous acid, is treated with an olefin at 0° to 20° C. These steps are repeated until the concentration of halohydrin reaches a value above which the formation of hypochlorous acid is depressed by the accumulated hydrochloric acid. The concentration of the latter should not exceed 1 molar and is maintained by addition of water and withdrawal of treated liquid. Anhydrous halohydrins are obtained by conversion into olefin oxide followed by treatment with dry hydrogen halide.

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[34] U. S. Patent 1,308,763, July 8, 1919; *Chem. Abs.*, 1919, **13**, 2218.

[35] U. S. Patent 1,394,664, Oct. 25, 1921; Canadian Patent 221,754, 1922; *Chem. Abs.*, 1922, **16**, 3316; assigned to Chadeloid Chemical Co. For the use of kerosene as a solvent for olefins in the manufacture of chlorohydrins, see Brooks, U. S. Patents 1,498,781 and 1,498,782, June 24, 1924; *Chem. Abs.*, 1924, **18**, 2600.

[36] Brooks, U. S. Patent 1,446,873, Feb. 27, 1923; assigned to Chadeloid Chemical Co.; *Chem. Abs.*, 1923, **17**, 1481.

[37] U. S. Patent 1,446,874, Feb. 27, 1923; assigned to Chadeloid Chemical Co.; *Chem. Abs.*, 1923, **17**, 1481.

[38] U. S. Patent 1,386,118, Aug. 2, 1921; *Chem. Abs.*, 1921, **15**, 3851.

[39] U. S. Patent 1,456,590, May 29, 1923; *Chem. Abs.*, 1923, **17**, 2428.

[40] U. S. Patents 1,456,916 and 1,456,959, May 29, 1923; *Chem. Abs.*, 1923, **17**, 2428; British Patent 235,044, 1924; *Brit. Chem. Abs.* B, 1925, 652.

[41] U. S. Patent 1,465,601, Aug. 21, 1923; assigned to Carbide and Carbon Chemicals Corp.

[42] British Patent 265,259, 1925; *Chem. Abs.*, 1928, **22**, 244.

Olefin chlorohydrins are obtained as intermediate products in the manufacture of 1,2-glycols prior to hydrolysis.[43] For example, in the production of ethylene glycol, 482 cubic feet of ethylene and 241 cubic feet of carbon dioxide are passed into a cold 5 per cent hypochlorite solution, containing 100 pounds of sodium hypochlorite. The ethylene is admitted in the form of fine bubbles while the carbon dioxide is introduced sufficiently slowly into the cooled liquid to maintain a low concentration of hypochlorous acid. The solution of ethylene chlorohydrin is then boiled for several hours to effect hydrolysis to the glycol. Polyhydroxy-compounds, e.g., glycerol from allyl alcohol, are made in a similar manner.[44]

In the process of Youtz,[45] ethylene is dissolved in an aqueous medium at a pressure of 100 to 200 atmospheres and the resulting solution, free from undissolved gaseous olefin, is allowed to react with hypochlorous acid. The application of pressure is also advocated by the T. Goldschmidt A.-G.[46]

Isham and Spring[46a] prepared chlorohydrins by treating an alkylene dichloride (ethylene dichloride) with sulphur trioxide at 35° to 45° C. and subsequently hydrolyzing the chloroethylsulphuric chloride. The chlorohydrin may be separated from the mixture by fractional distillation.

Another suggestion for preparing chlorohydrins consists in reacting esters of hypochlorous acid and tertiary alcohols with organic compounds containing one or more double bonds, such as olefins, diolefins, or oleic acid.[46b]

Recovery of Ethylene Chlorohydrin

Various methods have been proposed for recovering ethylene chlorohydrin from the comparatively dilute solutions obtained in its preparation. A constant-boiling mixture of ethylene chlorohydrin and water, containing 42.5 per cent chlorohydrin and 57.5 per cent water, boiling point 95.8° C. (735 mm.), is known.[47] When dilute aqueous solutions are distilled, it is a comparatively easy matter to obtain a distillate containing 20 to 25 per cent of chlorohydrin. Saturation of a 35 per cent solution of chlorohydrin with salt causes a separation into two layers, the oil layer containing about 70 per cent chlorohydrin. When this 70 per cent solution of chlorohydrin is distilled the azeotropic mixture first comes over, and finally anhydrous chlorohydrin, boiling point 128° to 128.5° C.[48] Other methods of obtaining pure chlorohydrin are distillation with benzene,[49] and extraction with organic solvents such as ether.[50] Another procedure which has been advanced is to convert the dilute chlorohydrin into ethylene oxide and then treat this compound with dry hydrogen chloride.[51]

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[43] Essex and Ward, U. S. Patent 1,594,608, Aug. 3, 1926; assigned to E. I. duPont de Nemours & Co., Inc.

[44] Essex and Ward, U. S. Patent 1,626,398, Apr. 26, 1927; assigned to E. I. duPont de Nemours & Co., Inc.

[45] U. S. Patent 1,875,309, Aug. 30, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, **26**, 5971. The use of lower pressures, 75 to 90 pounds per square inch, has been recommended by McElroy, U. S. Patent 1,510,790, Oct. 7, 1924; assigned to Carbide and Carbon Chemicals Corp., *J.S.C.I.*, 1925, 27B.

[46] British Patent 293,754, 1928; *Chem. Abs.*, 1929, **23**, 1651. German Patent 538,915, 1927; *Chem. Abs.*, 1932, **26**, 2198.

[46a] U. S. Patent 1,918,967, July 18, 1933; assigned to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 4815.

[46b] Bataafsche Petroleum Maatschappij, French Patent 740,350, 1932; *Chem. Abs.*, 1933, **27**, 2160.

[47] Gomberg, *J.A.C.S.*, 1919, **41**, 1414. Bancelin and Rivat (*Bull. soc. chim.*, 1919, **25**, 552) give the boiling point of the 42% constant boiling mixture as 97.85°C./760 mm.

[48] Brooks, *Chem. Met. Eng.*, 1920, **22**, 631.

[49] Kirst, U. S. Patent 1,386,118, Aug. 2, 1921; *Chem. Abs.*, 1921, **15**, 3851.

PROPERTIES OF ETHYLENE CHLOROHYDRIN

Ethylene chlorohydrin is a colorless liquid of d^{20}_{4} 1.1980, boiling at 132° C. at 761 mm and 51° to 52° C. at 22 mm. It forms a constant-boiling mixture with water (42.5 per cent chlorohydrin and 57.5 per cent water) which boils at 95.8° C. at 735 mm.[52]

Some of the physical constants of solutions of ethylene chlorohydrin in water and in saturated brine have been determined by Bozza and Gallarati.[53] The refractive index of aqueous solutions varies practically linearly with the composition by weight, the value (N^{20}_{D}) for pure chlorohydrin being 1.4421. Table 102 shows the boiling points of azeotropic mixtures in pure water and in saturated sodium chloride at various pressures.

TABLE 102.—*Boiling Point of Ethylene Chlorohydrin Azeotropes.*

Solvent	760 mm. ° C.	504 mm. ° C.	400 mm. ° C.
Water	97.8	86.4	80.55
Saturated sodium chloride solution in water	101.4	90.7	85.4

The azeotropic mixture from pure water solutions at 400 mm. pressure contains 40.5 per cent by weight of ethylene chlorohydrin, while that obtained from saturated brine at the same pressure contains 57.8 per cent. This displacement of composition of the azeotrope in the presence of sodium chloride makes possible the concentration of chlorohydrin solutions by alternate distillation from aqueous and sodium chloride solutions.

Anhydrous ethylene chlorohydrin possesses marked solvent properties but the ease with which it hydrolyzes with the formation of corrosive hydrochloric acid greatly restricts its usefulness.[54] Ethylene chlorohydrin is a solvent for cellulose acetate and the solutions have a high tolerance for water, while cellulose acetates containing over 50 per cent of combined acetic acid dissolve in equal parts of chlorohydrin and water.[55] This chlorohydrin is miscible with benzene, water and alcohol. It possesses marked toxic properties,[56] due probably to its hydrolysis in the tissues with the production of hydrochloric acid. It has been noted [57] that ethylene chlorohydrin possesses the power of shortening the dormant period of potato tubers and of inducing early sprouting and budding. Juice from potato tubers which were treated with 1.6 per cent of ethylene chlorohydrin, kept in a closed container for 24 hours and then planted in moist soil for 5 days, was found to contain glutathione,[57a] which cannot be found in untreated potatoes. This chlorohydrin increases the rate of hydrolysis of starch by the enzyme, amylase.[58]

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[50] Irvine and Haworth, U. S. Patent 1,496,675, June 3, 1924; assigned to Carbide and Carbon Chemicals Corp.; *J.S.C.I.*, 1924, 43, 693B.

[51] Long, Willson and Wheeler, British Patent 265,259, 1925; *Brit. Chem. Abs.* B, 1927, 347.

[52] Gomberg, *J.A.C.S.*, 1914, 41, 1414.

[53] *Giorn. chim. ind. applicata,* 1931, 13, 163; *Chem. Abs.*, 1931, 25, 3962.

[54] For the rates of hydrolysis of ethylene and propylene chlorohydrins see Brooks, *Chem. Met. Eng.*, 1920, 22, 631.

[55] Durrans, "Solvents," Chapman and Hall, London, 1930. Lindsay, U. S. Patent 1,226,340, May 15, 1917; assigned to The Celluloid Co.; *J.S.C.I.*, 1917, 36, 707. Webb, U. S. Patent 1,444,406, Feb. 6, 1923; assigned to Eastman Kodak Co.; *Chem. Abs.*, 1923, 17, 1329.

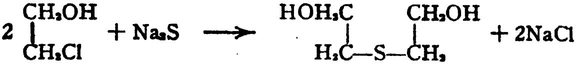
[56] Durrans, *Chem. Age (London)*, 1931, 24, 575.

[57] Denny, *Amer. J. Bot.*, 1926, 13, 386; *Chem. Abs.*, 1927, 21, 1137. Denny and Stanton, *Amer. J. Bot.*, 1928, 15, 327; *Chem. Abs.*, 1928, 22, 3194. Werner, *Nebraska Agri. Exp. Sta. Res. Bull.* 57, 1931; *Brit. Chem. Abs.* B, 1932, 318. Bramble, *Science*, 1932, 75, 193; *Brit. Chem. Abs.* B, 1932, 396. Miller, *Contr. Boyce Inst.*, 1931, 3, 321; *Brit. Chem. Abs.* A, 1931, 1466. Guthrie, Denny and Miller, *Contr. Boyce Inst.*, 1932, 4, 131; *Chem. Abs.*, 1932, 26, 6058.

The chemical properties of ethylene chlorohydrin are typical of those of the α-halohydrins as a class. All these substances possess a chemical reactivity which can be traced to the lability of the halogen atom in these compounds. The reactivity of the chlorine atom is not greatly affected by esterifying the hydroxyl group, a fact which is utilized in the manufacture of novocain by the action of diethylamine on the p-aminobenzoic ester. When the hydroxyl group and chlorine atom in chlorohydrins are separated by one or more CH_2 groups, the chemical reactivity of the halogen atom is reduced to approximately that of the alkyl chlorides.

Ethylene chlorohydrin is finding application as a chemical intermediate in the preparation of a number of synthetic products, particularly ethylene glycol,[59] ethylene oxide[60] and their derivatives. The glycol and the oxide result from the action of alkalies on ethylene chlorohydrin. Weak alkalies (e.g., sodium bicarbonate solutions) yield ethylene glycol, solid soda or potash furnish ethylene oxide, while dilute solutions of strong alkalies yield gummy condensation products of unknown nature. When hydrolyzed by water at 100° C., ethylene chlorohydrin yields acetaldehyde in addition to glycol.[61] Steimmig and Wittwer[61a] obtained an 80 per cent yield of ethylene glycol carbonate, a solid melting at 38.5° to 39° C.[61b] and boiling at 236° C., on heating equimolecular proportions of ethylene chlorohydrin and sodium bicarbonate for several hours.

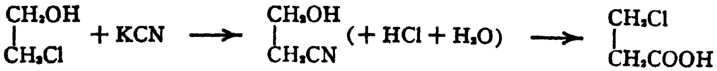
The activity of the halogen atom in ethylene chlorohydrin is demonstrated by the following reactions, which may be regarded as typical of α-chlorohydrins: (a) With sodium sulphide to give thiodiglycol,[62] a substance which was used in the preparation of mustard gas. A 79 to 86 per cent yield of β-thiodiglycol is obtained by treating 1500 grams of a 20 per cent aqueous solution of ethylene chlorohydrin with 750 grams of water containing 493 grams of sodium sulphide ($Na_2S.9H_2O$), with stirring, at 30° to 35° C. and then heating for 45 minutes at 90° to 95° C.[63]



$$2\;\begin{array}{l}CH_2OH\\ |\\ CH_2Cl\end{array} + Na_2S \longrightarrow \begin{array}{ccc}HOH_2C & & CH_2OH\\ | & & |\\ H_2C & -S- & CH_2\end{array} + 2NaCl$$

(b) With sodium iodide to furnish the corresponding iodohydrins.[64]

(c) With alkali cyanides to yield cyanohydrins. Thus, Jacobs and Heidelberger[65] by refluxing ethylene chlorohydrin with potassium cyanide in alcoholic solution for 8 hours, obtained ethylene cyanohydrin which, on treatment with concentrated hydrochloric acid, gave α-chloropropionic acid.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2Cl\end{array} + KCN \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2CN\end{array} (+ HCl + H_2O) \longrightarrow \begin{array}{l}CH_2Cl\\ |\\ CH_2COOH\end{array}$$

[57a] Guthrie, *J.A.C.S.*, 1932, 54, 2566.

[58] Clark, Fowler and Black, *Trans. Roy. Soc. Canada*, 1931, (3) 25, 99; *Brit. Chem. Abs.* **A**, 1932, 427.

[59] See Chapter 22.

[60] See Chapter 23.

[61] Krassuski, *J. Russ. Phys.-Chem. Soc.*, 1902, 34, 287; *Chem. Zentr.*, 1902, 2, 19.

[61a] U. S. Patent 1,907,891, May 9, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 3721.

[61b] See Nemirovaki, *J. prakt. Chem.*, 1883, (2) 28, 439; *Chem. Soc. Abs.*, 1884, 46, 419.

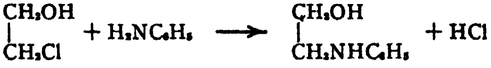
[62] Victor Meyer, *Ber.*, 1887, 19, 3259.

[63] Faber and Miller, "Organic Syntheses," 1932, 12, 68; *Chem. Abs.*, 1932, 26, 3484.

[64] Henry, *Ber.*, 1885, 18, 519. Butlerow, *Ann.*, 1867, 144, 42.

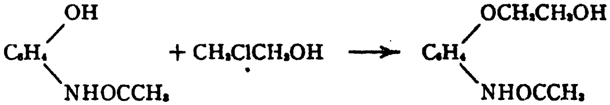
[65] *J.A.C.S.*, 1917, 39, 1465.

(d) With primary and secondary amines to give amino-alcohols, a reaction which has been employed for the manufacture of novocain. On reacting equimolecular proportions of aromatic di- or poly-amines with ethylene chlorohydrin in the presence of a solvent and an acid-binding agent, the mono-hydroxyalkyl derivatives are formed.[65a] Kamm, Adams and Volwiler,[66] by condensing ethylene chlorohydrin with dibutylamine and esterifying the product with p-aminobenzoic acid, have prepared a novocain-like substance containing a dibutylamino group instead of diethylamino. The reaction is also exemplified by the combination of ethylene chlorohydrin with aniline to yield β-anilinoethanol, which may be represented as:[67]

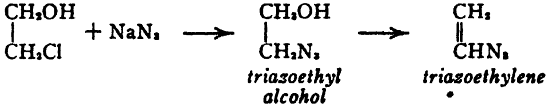


$$\begin{matrix} CH_2OH \\ | \\ CH_2Cl \end{matrix} + H_2NC_6H_5 \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2NHC_6H_5 \end{matrix} + HCl$$

(e) With alkali phenolates to form ethers of the type $C_6H_5OCH_2CH_2OH$. A somewhat similar reaction is that with p-hydroxyacetanilide to form p-β-hydroxyethoxyacetanilide.[68]

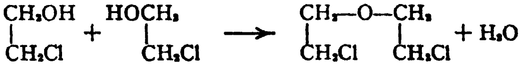


(f) With sodium azide to replace the chlorine atom by the triazo group.[69] The resulting triazoethyl alcohol has been made the starting point for the synthesis of triazoethylene, boiling point 26° C.



$$\begin{matrix} CH_2OH \\ | \\ CH_2Cl \end{matrix} + NaN_3 \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2N_3 \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CHN_3 \end{matrix}$$

(g) With concentrated sulphuric acid at 90° to 100° C. to result in a 75 per cent yield of ββ′-dichlorodiethyl ether,[70] an industrial solvent.



$$\begin{matrix} CH_2OH \\ | \\ CH_2Cl \end{matrix} + \begin{matrix} HOCH_2 \\ | \\ CH_2Cl \end{matrix} \longrightarrow \begin{matrix} CH_2\text{—}O\text{—}CH_2 \\ | \qquad\quad | \\ CH_2Cl \quad CH_2Cl \end{matrix} + H_2O$$

(h) The chlorohydrins may be esterified in some cases by the action of acid chlorides such as acetyl chloride. Ethers may also be produced by the substitution of the hydrogen atom of the hydroxyl group by alkyl groups. Thus by the action of dimethyl and diethyl sulphates on 1-chloro-2-hydroxypropane (propylene α-chlorohydrin) Dewael[71] has prepared the methyl and ethyl ethers, having the formulas $CH_2ClCH(OCH_3)CH_3$ and $CH_2ClCH(OC_2H_5)CH_3$, respectively.

UTILIZATION OF ETHYLENE CHLOROHYDRIN

The main use of ethylene chlorohydrin is as an intermediate in the production of ethylene glycol and its derivatives. To a much less extent it has been used in the manufacture of local anesthetics such as novocain. It reacts with aniline to form anilinoethanol (as previously mentioned), which in turn is converted into indoxyl (an intermediate in the synthesis of indigo) by alkali fusion.[72] On condensing ethylene chlorohydrin with a primary or secondary aliphatic amine containing at least one alkyl group with more than eight carbon atoms, products are formed which can be used as wetting, washing, and dispersing agents.[72a]

[65a] I. G. Farbenindustrie A.-G., British Patent 386,254, 1932; *Brit. Chem. Abs.* **B**, 1933, 220.
[66] U. S. Patent 1,358,750, Nov. 16, 1920; *Chem. Abs.*, 1931, 15, 412.
[67] Knorr, *Ber.*, 1889, 22, 2092. Otto, *J. prakt. Chem.*, 1891, (2) 44, 17.
[68] Tcherniac, Canadian Patent 195,615, 1919; *Chem. Abs.*, 1920, 14, 596; British Patent 120,081, 1917; *Chem. Abs.*, 1919, 13, 362.
[69] Forster and Newman, *J.C.S.*, 1910, 97, 2570.
[70] Kamm and Waldo, *J.A.C.S.*, 1921, 43, 2223.
[71] *Bull. soc. chim. Belg.*, 1930, 39, 395; *Chem. Abs.*, 1931, 25, 2416.

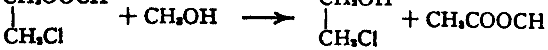
Another possible application is in the refining of oil fractions, such as brown-coal tar distillates. According to Steinbrecher,[73] paraffins and naphthenes may be separated from unsaturated and aromatic hydrocarbons, phenols, and sulphur and nitrogen compounds by this solvent.

Chlorohydrins are employed in the manufacture of hardenable resins by interaction with phenol alcohols, such as diphenylolpropanetetracarbinol.[74] Ellis and Weber [75] obtained a light-colored resin of low acid number by esterification of rosin with a mixture of ethylene and propylene chlorohydrins. On heating dimethylol urea in ethylene chlorohydrin to 90° C. in the presence of a small proportion of urea nitrate, neutralizing and treating the solution with ethyl alcohol, a precipitate separates. When heated in a solution of sodium linoleate to 120° C., this precipitate forms a resin resembling linoxyn which can be used in the manufacture of lacquers and plastics.[75a]

Dichlorodiethyl ether, $ClCH_2CH_2OCH_2CH_2Cl$, is a colorless liquid of boiling point 178° C., which on account of its stability and resistance to hydrolysis may be used as a high-boiling solvent It is not a solvent for the cellulose esters but in conjunction with 10 to 30 per cent of alcohol it becomes an active solvent, and has been suggested as a high-boiling diluent in lacquers.[76] This ether has also been incorporated in scouring soaps and in wetting-out agents and penetrants, especially in the treatment of cotton fabrics. Dichlorodiethyl ether has been used as a selective solvent in the refining of lubricating oils (Chlorex process),[76a] and has been proposed for the extraction of tar from pyroligneous liquids.[76b]

The chemical reactions of β,β'-dichlorodiethyl ether are similar to those of ethylene dichloride. Thus, on treatment with ammonia and amines, it yields amino-ethers and substituted amino-ethers. With sodium alcoholates or phenolates, chloralkyl or chloraryl ethers, as well as dialkyl or diaryl ethers of diethylene glycol, are formed.

Ethylene formochlorohydrin, CH_2ClCH_2OOCH, a colorless mobile liquid, boiling point 94° C. (760 mm.) and d^{1}_{4} 1.17, has been proposed as an intermediate in the production of pure ethylene chlorohydrin.[77] The chloroformate is prepared by saturating ethylene diformate with hydrogen chloride and fractionally distilling the mixture. Hydrolysis of the chloroformate with methyl alcohol (containing 1 per cent of hydrogen chloride) yields ethylene chlorohydrin.



$$\begin{array}{l} CH_2OOCH \\ | \\ CH_2Cl \end{array} + CH_3OH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} + CH_3COOCH$$

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[72] Badische Anilin- und Soda-Fabrik, German Patent 171,172, 1904; *Chem. Zentr.*, 1906, 2, 386.

[72a] I. G. Farbenindustrie A.-G., British Patent 358,114, 1930; *Brit. Chem. Abs.* B, 1932, 138.

[73] *Braunkohlenarch.*, 1930, No. 31, 1; *Chem. Abs.*, 1932, 26, 2848.

[74] Chemische Fabriken Kurt Albert G.m.b.H., French Patent 719,172, 1931; *Chem. Abs.*, 1932, 26, 3392.

[75] U. S. Patent 1,381,863, June 14, 1921; *Chem. Abs.*, 1921, 15, 3560.

[75a] Pungs, Eisenmann, Scholz and Kollmann, German Patent 540,071, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 1812.

[76] A discussion of the uses and properties of dichloroethyl ether is given by Fife and Reid, *Ind. Eng. Chem.*, 1930, 22, 513.

[76a] Page, Buchler and Diggs, *Ind. Eng. Chem.*, 1933, 25, 418; see Chapter 1.

[76b] Othmer, U. S. Patent 1,866,719, July 12, 1932; assigned to Eastman Kodak Co.; *Brit. Chem. Abs.* B, 1933, 580.

[77] Von Bichowsky, U. S. Patent 1,488,571, Apr. 1, 1924; *J.S.C.I.*, 1924, 43, 577B.

Ethylene bromohydrin, CH_2OHCH_2Br, is a substance which was formerly prepared by the action of hydrogen bromide[78] or of phosphorus tribromide[79] on ethylene glycol. Mokievski[80] showed that the direct combination of aqueous hypobromous acid and ethylene occurred more rapidly and gave better yields of halohydrin (up to 60 per cent of the theoretical) than in the case of the combination of hypochlorous acid and ethylene. He prepared the hypobromous acid with the aid of mercuric oxide but it was subsequently found that the treatment of ethylene with cold bromine water gave good yields of bromohydrin. This latter method was afterwards investigated by Read and Williams,[81] who were able to obtain as high as 54 per cent yields of ethylene bromohydrin. Later Read and Hook[82] found that the reaction velocity is greater as the products accumulate for the reaction in which dibromide is formed than for the reaction yielding bromohydrin. This result is probably related to the great difference in solubility of the dibromide and bromohydrin and to the separation of the dibromide as a distinct phase. In spite of this, however, the molecular ratio of bromohydrin to dibromide, which in the initial stages of the reaction is as high as 20:1, remained greater than unity throughout the range of concentration investigated. When the concentration of bromohydrin had reached 0.2*N*, the molecular ratio of bromohydrin to dibromide was about 10:1. The reaction is best carried out at 0° C., as raising the temperature decreases the reaction rate and at the same time the ratio of bromohydrin to dibromide formed is materially reduced. Reaction is accelerated by exposure to sunlight, which does not, however, affect the relative proportions of the products.

Ethylene bromohydrin is a colorless, mobile liquid, miscible with water in all proportions. It boils with slight decomposition at 146° to 150° C. at normal pressure, at 53.5° C. at 14 mm. and 48.5° C. at 13 mm. It has d^0_4 1.7902, d^{20}_4 1.7629, n^{20}_D 1.4915 and forms a constant-boiling mixture with water, boiling point 99.1° C. (762.4 mm.), containing 35.0 per cent of bromohydrin. It may be partly salted out by saturating its aqueous solution with sodium sulphate or other salts. Bromohydrin dissolves in most of the common organic solvents but not in light petroleum. The vapors of the pure substance and also of its aqueous solutions exert a painful irritant action on the eyes and nostrils shortly after inhalation. Ethylene bromohydrin is hydrolyzed by water more readily than the chlorohydrin. The hydrolysis is perceptible, though very slow, in the cold and is accelerated by warming and by the presence of acids and alkalies.[83]

Ethylene iodohydrin, CH_2OHCH_2I, results from the action of potassium iodide on the chlorohydrin.[84] It is an oil of boiling point 85° C. (25 mm.), and d^{20}_4 2.905. Sand[85] prepared this compound by treating a mercury-ethanol compound with iodine.

PROPYLENE CHLOROHYDRINS

Propylene combines with hypochlorous acid solutions much more readily than ethylene to yield a mixture of two isomeric chlorohydrins, namely, 1-hydroxy-2-chloropropane and 1-chloro-2-hydroxypropane, the latter being the predominating product.[86]

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[78] Henry, *Jahresberichte*, 1872, 304.

[79] Demole, *Ber.*, 1876, 9, 48.

[80] *J. Russ. Phys.-Chem. Soc.*, 1898, 30, 900; *Chem. Soc. Abs.*, 1899, 76 (1), 729.

[81] *J.C.S.*, 1917, 111, 240.

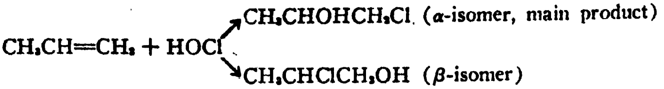
[82] *J.C.S.*, 1920, 117, 1214.

[83] Read and Hook, *loc. cit.*

[84] Butlerow and Ossokin, *Ann.*, 1867, 144, 42.

[85] *Ber.*, 1901, 34, 1385.

[86] Michael, *J. prakt. Chem.*, 1899, 60, 423; *Ber.*, 1906, 39, 2786; Henry, *Bull. acad. roy. Belg.*, 1906, 523; *Chem. Abs.*, 1907, 1, 2079; *Compt. rend.*, 1902, 134, 1070; *Chem. Zentr.*, 1902, I, 1316.



$$CH_3CH{=}CH_2 + HOCl \begin{cases} \nearrow CH_3CHOHCH_2Cl \text{ (α-isomer, main product)} \\ \searrow CH_3CHClCH_2OH \text{ (β-isomer)} \end{cases}$$

These chlorohydrins may be prepared in several other ways, for example from propylene glycol or oxide by treatment with hydrochloric acid. Smith,[87] from measurements of rates of hydrolysis of these products, has shown that most of them consist of a mixture of both isomers though the propylene chlorohydrin prepared from allyl bromide consists almost entirely of the α-isomer. Smith gives the figures in Table 103 for the proportions of the two isomers in propylene chlorohydrins prepared in various ways:

TABLE 103.—*Proportions of Isomers in Propylene Chlorohydrins.*

Mode of Preparation	Per Cent Composition α-isomer	β-isomer
From propylene glycol and S_2Cl_2	80	20
From propylene glycol and HCl at 140° C.	70	30
From propylene oxide	90	10
From propylene and HOCl	90	10

No systematic study is apparently available on the action of hypochlorous acid on propylene though methods have been developed for the production of mixtures of ethylene and propylene chlorohydrins from cracking gas by interaction with dilute solutions of hypochlorous acid.

Of the two propylene chlorohydrins, 1-hydroxy-2-chloropropane, d^{20}_4 1.103, boils at 133° to 134° C., and 2-hydroxy-1-chloropropane, d^{20}_4 1.111, boils at 126° to 127° C. The latter, which is the main product of the action of hypochlorous acid on propylene, may also be obtained by hydrating allyl chloride with the aid of sulphuric acid at 0° C.[88]

$$CH_2{=}CHCH_2Cl + H_2O \longrightarrow CH_3CHOHCH_2Cl$$

In chemical and physical properties the propylene chlorohydrins closely resemble ethylene chlorohydrin. Thus, heating with aqueous sodium bicarbonate converts both chlorohydrins into propylene glycol,[89] while heating with anhydrous caustic alkalies furnishes propylene oxide, the best results being obtained with little or no water in the reaction mixture. When 1-chloro-2-hydroxypropane is heated with water [90] at 140° to 160° C. or with zinc or lead oxides [91] a mixture of acetone and propionaldehyde is produced.

The propylene chlorohydrins are excellent solvents for certain grades of cellulose acetate, and for many copals and resins, but the ease of hydrolysis and the consequent formation of free hydrochloric acid militates against their extensive use as solvents. These substances are hydrolyzed by water to a slightly greater extent than ethylene chlorohydrin.[89]

The methods employed for making chlorohydrins (which have been previously reviewed) are in most instances applicable to propylene chlorohydrin. Apparently the use of dilute aqueous solutions of hypochlorous acid (e.g., from sodium hypochlorite and carbon dioxide) gives good results, especially if the olefin is absorbed under pressure.

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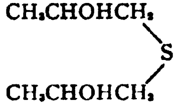
[87] *Z. physik. Chem.*, 1918, 93, 59; *Chem. Abs.*, 1919, 13, 1461.
[88] Bancroft, *J.A.C.S.*, 1919, 41, 424.
[89] Brooks, *Chem. Met. Eng.*, 1920, 22, 631.
[90] Krassuski, *J. Russ. Phys.-Chem. Soc.*, 1902, 34, 287; *Chem. Zentr.*, 1902, 2, 19.
[91] Eltekov, *J. Russ. Phys.-Chem. Soc.*, 1878, 10, 211; *Ber.*, 1878, 11, 989; *Chem. Zentr.*, 1878, 516.

A number of potentially valuable materials may be synthesized from propylene chlorohydrins by reactions similar to those undergone by ethylene chlorohydrin. Thus, for example, propylene chlorohydrin may be converted into a thiodiglycol, which is said to be valuable in dyestuff-printing. According to Kränzlein and Corell,[92] this thiodiglycol, or thiohydrin, which possesses the constitution:



may be prepared by introducing 189 parts of propylene chlorohydrin into 1000 parts of a normal solution of sodium sulphide. The mixture is heated to boiling for a short time, evaporated *in vacuo*, the sodium chloride separated out, and the thiohydrin distilled *in vacuo*. At 4 mm. the boiling point of propylene thiohydrin is 120° C.

By processes analogous to those already mentioned in the discussion of ethylene chlorohydrin, the propylene chlorohydrins may be converted into numerous other organic chemicals, e.g., into cyanohydrin by treatment with sodium cyanide or into amino-derivatives by condensation with amines.

BUTYLENE HALOHYDRINS

The halohydrins of the butylenes, amylenes and other olefins are not nearly so well known as the ethylene and propylene derivatives. As the series of hydrocarbons is ascended the number of possible isomers increases considerably. The chlorohydrins of the butylene series have been prepared mainly by the combination of olefin with dilute hypochlorous acid in the cold. Apparently there is an increasing tendency for dichlorohydrocarbons to be produced in the case of the higher olefins [93] in the presence of hypochlorous acid.

When butene-1 is treated with cold aqueous hypochlorous acid, some 1,2-dichlorobutane and trichlorobutane are formed. The main product is 1-chlorobutanol-2,

$$CH_3CH_2CHOHCH_2Cl$$

a colorless liquid of boiling point 141° C. On oxidation with chromic acid, this chlorohydrin yields chloromethyl ethyl ketone, a pungent liquid of boiling point 135° to 137° C. In the same way 1-bromobutanol-2 may be prepared from butene-1 and hypobromous acid. The bromohydrin is a colorless liquid, boiling at 56° to 58° C. (11 mm.), which also undergoes oxidation by chromic acid to a bromomethyl ethyl ketone.[94]

Ordinary butene, which consists mainly of butene-2, on treatment with a 1 per cent hypochlorous acid solution yields the chlorohydrin, 2-chlorobutanol-3, a liquid of boiling point 138° to 139° C., d_0^0 1.0868.[95] This substance when heated alone to 180° C., or with water at 120° C., is converted into methyl ethyl ketone and hydrochloric acid,

$$CH_3CHClCHOHCH_3 \longrightarrow CH_3CH_2COCH_3 + HCl$$

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[92] U. S. Patent 1,570,262, Jan. 19, 1926; assigned to Farbwerke vorm Meister, Lucius und Brüning; *Brit. Chem. Abs.* **B**, 1926, 218. British Patent 185,403, 1922; *J.S.C.I.*, 1923, **42**, 1118A.

[93] Muckermann, *J. prakt. Chem.*, 1911, **83**, 513.

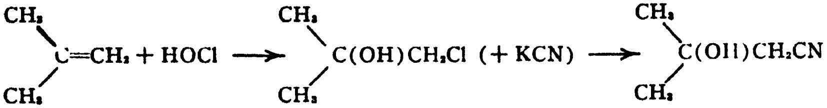
[94] deMontmollin and Matile, *Helv. Chim. Acta*, 1924, **7**, 106.

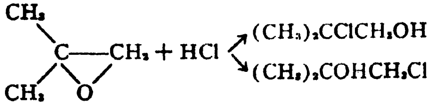
[95] Krassuski, *J. Russ. Phys.-Chem. Soc.*, 1901, **33**, 1; *Chem. Zentr.*, 1901, **1**, 995; Henry, *Compt. rend.*, 1907, **145**, 498, 763; *Chem. Zentr.*, 1907, **2**, 1489; Fourneau and Puyal, *Bull. soc. chim.*, 1922, (4) **31**, 424; *Chem. Abs.*, 1922, **16**, 2495.

According to Krassuski, isobutylene on treatment with hypochlorous acid yields mainly the chlorohydrin, 1-chloro-2-methylpropanol-2, boiling point 128° C., d_0^0 1.0878. This substance yields β-hydroxy-isovaleronitrile on treatment with potassium cyanide in alcohol. When isobutylene oxide reacts with hydrochloric acid this chlorohydrin is formed together with an isomer, namely 2-chloro-2-methylpropanol-1, boiling point 132° to 133° C. The relationship between these chlorohydrins is shown by the following scheme:

$$CH_3CH_2CH{=}CH_2 + HOCl \longrightarrow CH_3CH_2CHOHCH_2Cl$$

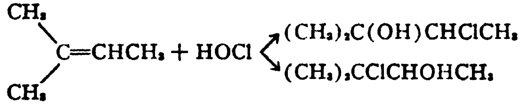
$$CH_3CH{=}CHCH_3 + HOCl \longrightarrow CH_3CHClCHOHCH_3$$





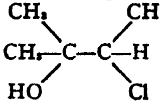
HALOHYDRINS OF THE HIGHER OLEFINS

Very little is definitely known about the higher alkylene chlorohydrins but combination between the higher olefins and hypochlorous acid appears to take place very readily with a tendency for chlorohydrocarbons to be produced. According to Krassuski [96] trimethylethylene combines with hypochlorous acid to yield two isomeric chlorohydrins, one of which is decomposed by refluxing with water to give isopropyl methyl ketone:



$$(CH_3)_2CClCHOHCH_3 \longrightarrow (CH_3)_2CCHCOCH_3 + HCl$$

The chlorohydrins of commercial amylene have been prepared by Walker,[97] who separated them from the accompanying hydrocarbons by fractional distillation and then converted them into a mixture of oxides by the action of alkalies. Kiss [97a] prepared aldehydes and ketones from olefins containing more than four carbon atoms by the action of hypochlorous acid on olefinic gasolines, the chlorohydrins thus formed being subsequently heated with water.

An interesting process for making chlorohydrins has been worked out by Detoeuf,[98] who used N-chlorourea as a source of hypochlorous acid. A solution of this compound in water, containing 10 per cent of urea hydrochloride or 5 per cent acetic acid, was shaken with the unsaturated hydrocarbon. A neutral solution of N-chlorourea reacts too slowly, and too acid solutions evolve chlorine. With this reagent Detoeuf was able to prepare the chlorohydrins of a number of olefins.[99] For example, from trimethylethylene a 70 per cent yield of the chlorohydrin  was obtained. This chlorohydrin reacted with potassium hydroxide to furnish the oxide, and with barium carbonate solution to produce the glycol. With aniline, a ketone was formed and this reaction is general in the case of the higher chlorohydrins:

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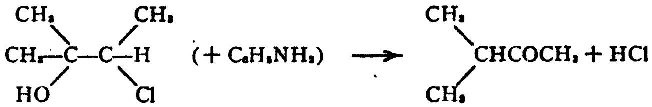
[96] *J. Russ. Phys.-Chem. Soc.*, 1901, 33, 1; *ibid.*, 1902, 34, 287; *Chem. Zentr.*, 1901, 1, 995; *ibid.*, 1902, 2, 19.

[97] U. S. Patent 972,952, Oct. 18, 1910; assigned to Maas and Waldstein Co.; *Chem. Abs.*, 1911, 5, 150.

[97a] U. S. Patent 1,767,291, June 24, 1930; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, 24, 4386.

[98] *Bull. soc. chim.*, 1922, 31, 102; *Chem. Abs.*, 1922, 16, 1395. N-chlorourea is prepared by the action of chlorine on urea in a little water at 0° C. The crystalline product is isolated by cooling the mixture with methyl chloride and filtering. See also Béhal and Detoeuf, *Compt. rend.*, 1911, 153, 681; *Chem. Abs.*, 1912, 6, 82.



It has been proposed to make amylene bromohydrins, which are said to be useful in the preparation of pharmaceutical products, by the action of hypobromites on amylene in the presence of weak acids such as boric acid.[100]

Two chlorohydrins of the hexene series have been described by Henry.[101] One of these is obtained (accompanied by some dichloride) by the action of hypochlorous acid on hexene-2 (from mannite), and probably has the constitution,

$$CH_3CHOHCHClCH_2CH_2CH_3.$$

This is a liquid of boiling point 170° C. and d^{11}_4 1.018 and is converted by the action of acetyl chloride into hexylene acetochlorohydrin. An isomeric halohydrin, prepared by the action of hydrochloric acid on hexylene oxide, probably possesses the formula,

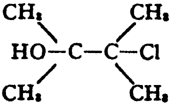
$$CH_3CH_2CH_2CHOHCHClCH_3.$$

This chlorohydrin is a colorless liquid, insoluble in water, and of d^{11}_4 1.0143. The corresponding bromohydrin is a colorless liquid of penetrating odor, insoluble in water, and of boiling point 188° to 190° C. (769 mm.) and d^{11}_4 1.2959. The corresponding iodohydrin was also prepared by Henry.

According to Detoeuf[102] the action of N-chlorourea in aqueous solution on hexene-2 furnishes a chlorohydrin having the formula,

$$CH_3CH_2CH_2CHOHCHClCH_3.$$

The product is obtainable in a 60 per cent yield although the reaction is very slow. On treatment with potassium hydroxide the oxide is formed, and in the presence of barium carbonate it is hydrolyzed to the glycol. In the same manner the chlorohydrin of tetramethylethylene has been prepared by Detoeuf in 67 per cent yield. This chlorohydrin possesses the structure:



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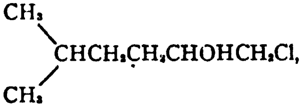
[99] *Bull. soc. chim.*, 1922, 31, 169, 176; *Chem. Abs.*, 1922, 16, 2113.
[100] Rath, German Patent 301,905, 1918; *Chem. Abs.*, 1919, 13, 363.
[101] *Compt. rend.*, 1883, 97, 260; *Chem. Soc. Abs.*, 1884, 46, 33.
[102] *Bull. soc. chim.*, 1922, 31, 169, 176; *Chem. Abs.*, 1922, 16, 2113.

and, in the presence of alcoholic potassium hydroxide, yields 90 per cent of the corresponding oxide.

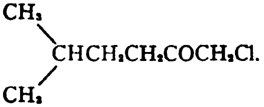
Detoeuf has succeeded in preparing a number of the higher chlorohydrins, of which the following may be mentioned:

Isoheptylene chlorohydrin,



$$\begin{matrix} CH_3 \\ & \diagdown \\ & & CHCH_2CH_2CHOHCH_2Cl, \\ & \diagup \\ CH_3 \end{matrix}$$

was obtained in an 85 per cent yield from isoheptene-1. It is a liquid of boiling point 97° to 98° C. (23 mm.), d^0_4 1.044, n^{14}_D 1.45662 and on oxidation yields a ketone[103] of the formula,



$$\begin{matrix} CH_3 \\ & \diagdown \\ & & CHCH_2CH_2COCH_2Cl. \\ & \diagup \\ CH_3 \end{matrix}$$

Octene-2 chlorohydrin, ($CH_3CH_2CH_2CH_2CH_2CHOHCHClCH_3$), is obtainable in 50 per cent yield from octene-2 and aqueous N-chlorourea. It is a liquid of boiling point 99° to 110° C. (14 mm.), d^0_4 1.001, n^{19}_D 1.45232 and, on oxidation furnishes α-chloromethyl hexyl ketone.

Styrene chlorohydrin, ($C_6H_5CHOHCH_2Cl$), can be made from styrene in a similar way, and has a boiling point of 128° C. (17 mm.), d^0_4 1.225, n^D_{17} 1.55405. On oxidation it is converted into a chloroketone,

$$C_6H_5COCH_2Cl.$$

Potassium hydroxide converts it into the oxide, while sodium ethylate reacts with it to yield an ether.

Cyclohexene chlorohydrin is the result of the reaction between cyclohexene and N-chlorourea. It is a liquid, boiling point 84° to 85° C. (16 mm.), d^0_4 1.138, and n^{20}_D 1.44097. Treatment with potassium hydroxide furnishes the oxide, while oxidation gives 2-chlorocyclohexanone.

Detoeuf has laid down the following rules which, he believes, govern the addition of hypochlorous acid to the higher olefins: (1) When the carbon atoms of the double bond are unequally substituted, the hydroxyl group becomes attached to the more substituted carbon atom. (2) When these carbon atoms are equally substituted, the hydroxyl group becomes attached to the carbon atom farthest from the end of the chain.

In regard to the elimination of hydrogen chloride from the higher chlorohydrins, Detoeuf enumerates the following rules: (1) If the medium is alkaline and the temperature low, oxides are formed. (2) If the medium is alkaline and the temperature high, conversion to a ketone takes place, often with intramolecular change. (3) If the medium tends to become acid (e.g., by dissociation of aniline hydrochloride when aniline is employed), a ketone is formed. (4) In neutral solution hydrolysis to the glycol occurs.

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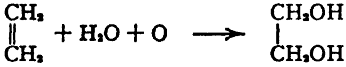
[103] For the action of chlorous anhydride on heptylene, see Grissom, *Amer. Chem. J.*, 1888, **10**, 225.

Chapter 22

Production, Properties and Uses of Simple Glycols

The glycols, or dihydric alcohols, derived from the olefins contain two hydroxyl groups attached to adjoining carbon atoms in the chain and are referred to as α- or 1,2-glycols. Although ethylene glycol, the simplest and most important member of the series, was discovered as early as 1857 by Wurtz,[1] this material was merely a laboratory product until about 1925. There has been an extraordinary revival of interest in the glycols and their derivatives and these substances are finding numerous and important applications in chemical and other industries. The commercial development and large-scale production of the glycols, and especially of ethylene glycol, is undoubtedly due, in large measure, to the availability of large supplies of cheap ethylene (and its immediate homologues) as by-products in the cracking of higher petroleum fractions.

The conversion of olefins into glycols, which is exemplified by ethylene as follows:



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + O \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

is an oxidation process. Although the earlier workers in this field of synthesis (as well as the later commercial processes) employed intermediate compounds, such as the dihalides or chlorohydrins, to effect this conversion, attempts have been made to convert olefins directly into glycols by the action of oxidizing agents (Chapter 39). The direct methods of adding two hydroxyl groups to the double bond involve the use of such oxidizing agents as dilute potassium permanganate and concentrated persulphuric acid (or Caro's acid, H_2SO_5) or of such catalysts as osmium tetroxide. The earliest direct oxidation of unsaturated compounds to glycols was accomplished by Tanatar,[2] who prepared a tartaric acid from fumaric acid by the use of dilute aqueous potassium permanganate. Somewhat later Saytzeff[3] showed that the same reagent could be used to convert oleic and elaidic acids to dihydroxystearic acid. The hydroxylation of crotonic and cinnamic acids (also with potassium permanganate) was effected by Fittig.[4] That this reagent might be employed to convert unsaturated hydrocarbons into glycols was first demonstrated by Wagner,[5] who prepared in this way the glycols of ethylene, isopropylethylene, isobutylene and trimethylethylene as well as glycerol from allyl alcohol and ethylglycerol from ethylvinylcarbinol. A number of other investigators[6] have shown that dilute potassium permanganate converts mesityl oxide, unsaturated acids, and terpene hydrocarbons into glycols.

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[1] *Ann.*, 1857, 104, 174; *ibid.*, 1858, 108, 84; *Compt. rend.*, 1857, 45, 228; *ibid.*, 1858, 47, 346; *Ann. chim. phys.*, 1859, (3) 55, 400; *Bull. soc. chim.*, 1859 1, 79; see Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1859, 13, 422.

[2] *Ber.*, 1879, 12, 2293.

[3] *J. Russ. Phys.-Chem. Soc.*, 1885, 17, 417; *Chem. Soc. Abs.*, 1886, 50, 140; *J. pr. Chem.*, 1886, (2) 33, 304.

[4] *Ber.*, 1888, 21, 920.

[5] *Ber.*, 1888, 21, 1230, 3343, 3347.

A reagent mentioned above which has been used with success to add two hydroxyls to the double bond is persulphuric acid or its primary decomposition product, Caro's acid. With this latter reagent Albitzsky[7] prepared dihydroxystearic acid from oleic and elaidic acids. Swann[8] converted allyl alcohol into glycerol and cyclohexene into trans-1,2-cyclohexanediol by the action of dilute aqueous solutions of persulphuric acid.

Another method of hydroxylating double bonds was discovered by Hofmann, Ehrhart and Schneider,[9] who succeeded in oxidizing ethylene to glycol and allyl alcohol to glycerol by the action of osmium tetroxide in the presence of an oxidizing agent (potassium chlorate). The method was improved for the oxidation of fumaric or maleic acids to tartaric acid by Milas and Terry.[10]

PRODUCTION OF ETHYLENE GLYCOL

Ethylene glycol was first prepared by Wurtz[11] from ethylene dibromide by reaction with anhydrous sodium acetate. The glycol diacetate thus formed was subsequently hydrolyzed to glycol. For the large-scale production of ethylene glycol two principal processes have been used industrially, namely, (1) the hydrolysis of ethylene dichloride, and (2) the hydrolysis of ethylene chlorohydrin. Another procedure involves the production of ethylene oxide from chlorohydrin, followed by hydration of the oxide to the glycol. These processes are discussed separately in this chapter.

The hydrolysis of ethylene dichloride takes place in the presence of alkalies, such as sodium carbonate, with the production of glycol but, unless conditions are carefully adjusted, the formation of other products, such as vinyl chloride, also occurs. With strong alkalies, vinyl chloride and acetylene result, and heating with water and lead oxide leads to the formation of glycol and aldehyde.[12]

Brooks and Humphrey[13] showed that conversion of the dichloride to glycol proceeds readily when the dichloride is heated under pressure with an alkali formate, ethylene diformate being an intermediate product. The process is carried out[14] by heating the dichloride with 1.25 to 2 times the theoretical amount of sodium formate in 3 to 5 volumes of methyl alcohol to 180° C. in an autoclave under a pressure of 260 pounds per square inch. At the end of the reaction, the liquid mixture is filtered to remove salt and then distilled first under ordinary pressure to remove methyl alcohol and methyl formate and then *in vacuo* to recover glycol.

Matter[15] proposed to hydrolyze ethylene dichloride by heating it in a closed vessel with an aqueous alkali bicarbonate solution in the presence of sheet copper as a catalyst. For example, 100 parts by weight of ethylene dichloride are heated with a solution of 180 parts of sodium bicarbonate in 1900 parts of water in a closed vessel during 6 hours at 130° to 140° C., the liquid being stirred continuously and a sheet of copper being used as catalyst. After cooling, the liquid is neutralized (e.g., with hydrochloric acid), concentrated, and fractionally distilled. In this way about 50 to 55 parts by weight of glycol are obtained.

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[6] Fittig, *Ann.*, 1892, 268, 3, 33; Harries and Pappos, *Ber.*, 1901, 34, 2979; Wagner, *Ber.*, 1894, 27, 1644.

[7] *J. Russ. Phys.-Chem. Soc.*, 1902, 34, 810; *Chem. Soc. Abs.*, 1903, 84 (1), 228.

[8] *Univ. Illinois Bulletin* 204, 1930, 27 (31); *Chem. Abs.*, 1930, 24, 2988.

[9] *Ber.*, 1913, 46, 1657.

[10] *J.A.C.S.*, 1925, 47, 1412.

[11] *Loc. cit.*

[12] Eltekoff, *Ber.*, 1878, 11, 989; *Chem. Soc. Abs.*, 1879, 36, 34.

[13] *Ind. Eng. Chem.*, 1917, 9, 750.

[14] Brooks and Humphrey, U. S. Patent 1,215,903, Feb. 13, 1917; assigned to Gulf Refining Co.; *Chem. Abs.*, 1917, 11, 1259.

[15] U. S. Patent 1,237,076, Aug. 14, 1917; *Chem. Abs.*, 1917, 11, 2904.

According to Engelhardt[16] ethylene glycol is produced by heating ethylene dihalides with concentrated aqueous solutions of salts having a feebly alkaline reaction, such as sodium, potassium, or calcium acetate, potassium oxalate, sodium phosphate or potassium benzenesulphonate. Neutralizing agents (sodium or potassium carbonate) can be added continuously or intermittently to maintain the solution slightly alkaline. Hibbert[17] proposed to make glycols by heating the olefin dichloride with an aqueous solution of sodium carbonate at 150° to 200° C. in an apparatus capable of withstanding considerable pressure.

Hydrolysis of dichlorides with aqueous solutions of the calcium salt of a weak acid under pressure at temperatures of 100° to 150° C. in a closed vessel has also been suggested. The use of calcium carbonate for this purpose has been recommended by McElroy.[18] When the calcium salts of acetic, lactic, butyric, formic and tartaric acids are employed, the corresponding glycol esters are produced.

The production of mixed glycols from mixed olefin dichlorides by this process can be carried out as follows: The dichlorides are mixed with an equal amount of finely powdered calcium carbonate and enough water to render the mass pasty. The mixture is heated to 115° to 130° C. for 2 to 3 hours in a closed container fitted with agitators. The glycols are recovered from the reaction product by steaming out in a manner analogous to that used for the recovery of glycerol. By heating 100 parts of dichloride with 180 to 190 parts of commercial calcium acetate and 350 to 500 parts of water to 120° to 150° C. for 3 to 4 hours, glycol diacetate is obtained. With 90 parts of calcium acetate, 50 parts of calcium carbonate and 100 parts of dichloride, the monoacetate of the glycol results.

In the process of Rodebush,[19] ethylene glycol is produced by heating 10 parts of ethylene dichloride, 10 parts of sodium carbonate, 2 parts of sodium acetate, and 15 parts of ethyl alcohol at 150° C. under 175 pounds per square inch pressure in the presence of excess of water. Britton[20] used ethylene chlorobromide as an intermediate in the production of the glycol. Approximately 2 parts by weight of ethylene chlorobromide and 3 parts of sodium carbonate were heated in a closed container with 29 parts of water at 145° C. for 4 hours. An almost theoretical yield of the glycol, based on the chlorobromide decomposed, was said to result.

Maier[21] made ethylene glycol by saponification of the dichloride with water at temperatures above 120° C. under pressure, the hydrochloric acid formed being neutralized by the continuous addition of an alkali or an appropriate metallic oxide. At the end of the reaction, most of the water was distilled off, and the glycol was extracted from the residue with alcohol. In another procedure Maier[22] converted the olefin dihalide into an organic ester (the diacetate), which is subsequently hydrolyzed by excess water under pressure at temperatures above its boiling point.

The production of glycol-glycerol mixtures was effected by Schlegel, Arnold, Arnold and Arnold[23] by reaction of ethylene dichloride with spent lyes from the manufacture of soap, the alkali content of the lye having been first converted into carbonate or bicarbonate by carbon dioxide evolved in a previous hydrolysis.

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[16] German Patent 410,857, 1917; assigned to Farbenfabriken vorm. F. Bayer und Co.; *J.S.C.I.*, 1925, 44, 568B.

[17] U. S. Patent 1,270,759, June 25, 1918; *J.S.C.I.*, 1918, 37, 531A.

[18] U. S. Patents 1,259,757 and 1,259,758, March 19, 1918; *Chem. Abs.*, 1918, 12, 1469; Canadian Patent 186,633, 1918; *Chem. Abs.*, 1918, 12, 2325.

[19] U. S. Patent 1,402,317, Jan. 3, 1922; *Chem. Abs.*, 1922, 16, 934.

[20] U. S. Patent 1,709,605, April 16, 1929; assigned to Dow Chemical Co.; *Chem. Abs.*, 1929, 23, 2724.

[21] French Patent 656,651, 1928; *Chem. Abs.*, 1929, 23, 4231; German Patent 537,448, 1927; *Chem. Abs.*, 1932, 26, 993.

[22] French Patent 697,171, 1930; *Chem. Abs.*, 1931, 25, 2739.

[23] German Patent 487,103, 1925; *Chem. Abs.*, 1930, 24, 2140.

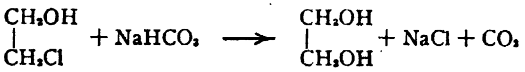
It has been known since 1873 that the olefin dihalides can be slowly hydrolyzed by water alone, but the reaction requires temperatures of the order of 170° C., or long periods of time at lower temperatures.[24] Bahr and Zieler[25] studied the hydrolysis of ethylene dichloride by water alone at various temperatures. Titration of the samples after heating for 1 hour gave the following conversions into glycol: at 160° C., 8 per cent; at 170° C., 18 per cent; and at 180° C., 34 per cent. The conversions obtained at various time intervals at 170° C. and 180° C., respectively, are given in Table 104.

Table 104.—*Hydrolysis of Ethylene Dibromide to Glycol.*

Time in Hours	At 170° C.	At 180° C.
	Per Cent	
0.5	8	—
0.75	—	31
1.0	18	34
1.5	—	41
2.0	28	—
2.5	—	61

It was shown that aldehydes began to be formed in quantity if the hydrochloric acid content of the liquid exceeded 1 per cent. A method of autoclave treatment was therefore adopted, which included addition of alkali at intervals to neutralize the excess hydrochloric acid. At 150° to 170° C., yields of 70 per cent were obtained with only small amounts of aldehyde or vinyl chloride. A loss of 20 to 25 per cent was attributed to volatilization or resinification of aldehyde. On a larger scale a yield of 1.5 to 2.0 kilograms of glycol per hour per 100 liters of reacting liquid resulted with a mixture containing 4 to 5 per cent of ethylene dichloride.

A number of processes use ethylene chlorohydrin as the starting material for the manufacture of glycol. The hydrolysis of ethylene chlorohydrin is effected, for the most part, with aqueous solutions of weak alkalies, such as sodium bicarbonate, according to the reaction:



$$\begin{matrix} CH_2OH \\ | \\ CH_2Cl \end{matrix} + NaHCO_3 \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + NaCl + CO_2$$

The use of anhydrous caustic alkalies results in the formation of olefin oxides, whereas more dilute caustic alkalies promote the formation of tarry non-distillable materials. Brooks[26] stated that when aqueous solutions of ethylene or propylene chlorohydrins are heated with aqueous sodium bicarbonate solutions, marked evolution of carbon dioxide ensues at about 65° C. By refluxing with sodium carbonate or bicarbonate solutions, yields of glycol are 44 to 48 per cent of the theoretical, the remainder being converted into olefin oxides which, on account of their volatility, are lost. By carrying out the reaction in a closed autoclave at 105° to 110° C. for 2 hours, yields of glycol of 90 per cent may be obtained. The remaining 10 per cent is converted into tarry material which cannot be distilled without decomposition, even under 10 mm. pressure. Calcium or magnesium hydroxides are not satisfactory for the hydrolysis as they firmly retain the glycol.

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[24] Eltekow, *Ber.*, 1873, 6, 158; *Chem. Soc. Abs.*, 1873, 26, 1016.
[25] *Z. angew. Chem.*, 1930, 43, 286; *Chem. Abs.*, 1930, 24, 3213.
[26] *Chem. Met. Eng.*, 1920, 22, 631.

The hydrolysis of ethylene chlorohydrin to produce glycol was described by Curme and Young.[27] A solution of caustic soda (about 20 per cent NaOH) is introduced into a kettle, and carbon dioxide is admitted in the cold, thus producing a solution of sodium bicarbonate. When the sodium hydroxide has been converted into bicarbonate, a charge of chlorohydrin solution (containing the precise amount of chlorohydrin necessary for complete reaction with the bicarbonate) is added to the bicarbonate solution in the kettle. The temperature of the reacting liquid is raised to 70° to 80° C., stirring meanwhile, and the hydrolysis is completed in about 4 to 6 hours. A further quantity of sodium hydroxide equivalent to a second charge of chlorohydrin, is treated in a second kettle with carbon dioxide derived from the reaction in the first. The carbon dioxide liberated entrains a considerable quantity of chlorohydrin which is thus wholly recovered by the absorption of gas in the caustic solution for the next operation. The reaction mixture is heated until evolution of carbon dioxide ceases and the charge is then withdrawn and a further quantity of caustic soda solution introduced while a new charge of chlorohydrin solution is added to the bicarbonate in the second kettle, and the process proceeds as before. It is stated that it is best to employ a 40 per cent chlorohydrin solution and to regulate the concentration of the alkali so that the actual chlorohydrin concentration in the reaction liquid at the beginning of the hydrolysis approximates 20 per cent.

Later, Curme[28] proposed to hydrolyze chlorohydrins with a solution of caustic alkali under such conditions that any appreciable escape of the intermediate olefin oxide is prevented, e.g., by using a vessel completely filled with liquid. The process may be made continuous. Calcium carbonate or a solution of calcium bicarbonate has been suggested by Oehme[29] for the hydrolysis of ethylene chlorohydrin.

Saunders and Wignall[30] described a continuous process for the vapor-phase hydrolysis of ethylene chlorohydrin to glycol or ethylene oxide by a solution of sodium carbonate or sodium hydroxide. At the bottom of a scrubber tower, lagged and filled with packing, a steady stream of steam enters and ascends against a descending flow of crude weak chlorohydrin solution. The amount of steam is adjusted so that it is exactly sufficient to volatilize and carry upwards the ethylene chlorohydrin contained in the solution. The current of steam laden with chlorohydrin traverses a fractionating column and passes away at the top, carrying 95 per cent of the chlorohydrin contained in the crude solution. The vapor then passes down a well-lagged pipe to the bottom of a second packed tower, which it enters by bubbling through hot liquid at the bottom. The admixed ethylene chlorohydrin vapors and steam ascending this tower meet a down-flowing solution of sodium carbonate (if ethylene glycol as such is to be obtained) or of caustic soda (if ethylene oxide is desired) admitted in the correct proportion. The ethylene chlorohydrin is hydrolyzed to the glycol with concomitant production of salt (NaCl), while steam, carbon dioxide, and volatile unhydrolyzable impurities pass away to a first condenser. The ethylene glycol dissolves in the salt solution and is carried down to the bottom of the tower and then flows from the trap direct to a desalter. The water and oily impurities are collected in a catch-pot where they form two layers. The oil is drawn off at the bottom and the water overflows at the top into the gas-separator. When ethylene oxide is formed it passes away at the top of the tower and can be dried and collected.

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[27] U. S. Patent 1,442,386, Jan. 16, 1923; assigned to Union Carbide Co.; *Chem. Abs.*, 1923, **17**, 1029.

[28] U. S. Patent 1,695,250, Dec. 11, 1928; *Chem. Abs.*, 1929, **23**, 610; British Patent 264,124, 1926; *Chem. Abs.*, 1928, **22**, 92; German Patent 540,513, 1926; *Chem. Abs.*, 1932, **26**, 2202; Canadian Patent 268,570, 1927; *Chem. Abs.*, 1927, **21**, 2274; all patents assigned to Carbide and Carbon Chemicals Corp.

[29] French Patent 612,825, 1926; assigned to Chem. Fabrik Kalk G.m.b.H.; *Brit. Chem. Abs.* **B**, 1928, 886.

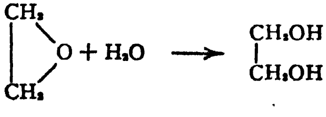
[30] U. S. Patent 1,737,545, Nov. 26, 1929; British Patent 286,850, 1927; *Chem. Abs.*, 1929, **23**, 397; both patents assigned to British Dyestuffs Corp., Ltd.

Another method for the production of glycols direct from olefins such as ethylene, propylene, or aryl-substituted alkylenes (e.g., styrene) is described by Essex and Ward.[31] The olefin is introduced, together with carbon dioxide, into a cold 5 per cent sodium hypochlorite solution. The resulting chlorohydrin solution is then heated under a reflux condenser for several hours to obtain the glycol. In this manner ethylene glycol can be obtained from ethylene; phenylglycol, from styrene; and glycerol, from allyl alcohol. The production of glycols with sodium hypochlorite has also been described by Blanchet.[32]

Dunstan and Birch[33] proposed a process for the manufacture of ethylene glycol in which an aqueous solution of ethylene chlorohydrin is mixed continuously with an aqueous solution of a non-caustic alkali (e.g., sodium carbonate) and heated to 105° to 150° C. under pressure. The hot reaction mixture is allowed to flow, under pressure at reaction temperature, through a series of heated "U" tubes, the rear limbs of which are packed and the forward limbs provided with downward-sloping baffles.

A method for the extraction of ethylene glycol or its homologues from aqueous solutions containing calcium or magnesium chlorides (such as are obtained in the hydrolysis of chlorohydrins by aqueous solutions or suspensions of lime or magnesia) is described by Oehme.[34] The mixture is distilled *in vacuo* at 250° to 400° C. with continuous stirring, or the liquid may be passed, after preliminary evaporation, through a tubular vacuum evaporator with a final temperature of 280° to 320° C. Anhydrous calcium (or magnesium) chloride is recovered and the distillate, containing 25 to 35 per cent of glycol, is further rectified.

Closely allied with the above processes are those which involve the hydration of ethylene oxide, previously prepared from ethylene chlorohydrin, e.g., by treatment with anhydrous (or concentrated aqueous) alkali. The conversion of ethylene oxide into glycol by hydrolysis with water is easily carried out by heating in a closed vessel.[35] The reaction is accelerated by the addition of mineral acids, especially sulphuric acid.[36] In large-scale practice, the considerable heat evolution (about 25 kg. cals. per mole) must be considered. It has been proposed to effect the hydration of ethylene oxide according to the reaction



$$\begin{matrix} CH_2 \\ | \quad \diagdown \\ | \quad\; O \\ | \quad \diagup \\ CH_2 \end{matrix} + H_2O \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

in the presence of dilute sulphuric acid as a catalyst.[37]

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[31] U. S. Patent 1,594,608, Aug. 3, 1926; *Chem. Abs.*, 1926, 20, 3170; U. S. Patent 1,626,398, April 26, 1927; *Chem. Abs.*, 1927, 21, 2136; both patents assigned to E. I. duPont de Nemours and Co., Inc.

[32] French Patent 610,434, 1925; *Brit. Chem. Abs.* **B**, 1929, 10; see also British Patent 251,652, 1925; *Chem. Abs.*, 1927, 21, 1546; both patents assigned to Soc. anon. d'explosifs et de produits chimiques.

[33] British Patent 365,589, 1930; assigned to Anglo-Persian Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 494; also French Patent 725,150, 1931; *Chem. Abs.*, 1932, 26, 4827.

[34] British Patent 352,651, 1930; assigned to Chem. Fabrik Kalk G.m.b.H.; *Chem. Abs.*, 1932, 26, 5314.

[35] Wurtz, *Ann.*, 1860, 113, 255.

[36] Bigot, *Ann. chim.*, 1891, (6) 22, 448; *Chem. Soc. Abs.*, 1893, 64 (1), 3; Henry, *Compt. rend.*, 1907, 144, 1404; *Chem. Soc. Abs.*, 1907, 92 (1), 745.

[37] Oehme, German Patent 416,604, 1923; assigned to Chem. Fabrik Kalk G.m.b.H.; *Brit. Chem. Abs.* **B**, 1926, 108; Untiedt, U. S. Patent 1,641,710, Sept. 6, 1927; *Chem. Abs.*, 1927, 21, 3368.

According to Youtz,[38] glycols may be obtained by mixing olefin oxides with excess of water (20 molar proportions of the latter to one of olefin oxide) and a hydrolyzing catalyst and then heating above the boiling point of the olefin oxide. The use of a large excess of water is said to suppress the simultaneous formation of polyglycols.

Attention has already been directed to the possibility of directly oxidizing ethylene in the presence of water to yield ethylene glycol (see also Chapter 39). Skärblom[39] proposed to manufacture ethylene glycol from ethylene by introducing a mixture of ethylene and oxygen into water containing iodine (or a compound of iodine in which the iodine is combined sufficiently loosely to react with the ethylene in the presence of oxygen, for example, hydrogen iodide, ethylene diiodide, potassium triiodide or ferric triiodide). The reaction is carried out in the presence of a salt of iron or manganese or other oxidation catalyst. A similar method[39a] for preparing ethylene glycol consists in reacting air and water with ethylene at 150° to 300° C. under pressure, using antimony, lead, bismuth, silver, nickel, tin or arsenic as catalysts.

Electrolysis of an alkali metal hydroxide solution of an olefin under pressures of about 20 to 200 atmospheres has been proposed by Youtz[40] for the production of glycol. Hydrogenation of lactones also yields glycols.[40a]

CHEMICAL AND PHYSICAL PROPERTIES OF ETHYLENE GLYCOL

Ethylene glycol is a colorless, odorless liquid with a sweet taste. It melts[41] between —17.4° C. and —11.5° C. (indefinite because of tendency to supercool[42]), boils at 197.5° C. at 760 mm., and has a density of 1.115 at 20° C. It is miscible in all proportions with water, alcohol and many organic solvents, and 100 parts of ethyl ether dissolve 1.1 parts of glycol. Although in its general physical properties it bears a striking resemblance to glycerol on one hand and ethyl alcohol on the other, it differs from them in several particulars. Thus, for example, it is less viscous than glycerol and can be distilled without decomposition at atmospheric pressure.[43] In the anhydrous state it is exceedingly hygroscopic. There is some evidence for the existence of a dihydrate.[44]

The chemical properties of this glycol are those expected of a dihydric alcohol. Thus, it forms both mono- and di-esters which may be conveniently prepared from ethylene dichloride or chlorohydrin. A large number of ethers and ether-esters are also known, some of which are discussed more fully later. The ethers are conveniently produced by condensation of alcohols or phenols with ethylene oxide. Both mono- and di-metallic derivatives of glycol are known.[45]

[38] U. S. Patent 1,875,312, Aug. 30, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, **26**, 5962.

[39] British Patent 369,141, 1931; *Brit. Chem. Abs.* **B**, 1932, 670; French Patent 722,000, 1931; *Chem. Abs.*, 1932, **26**, 4067. German Patent 561,049, 1930; *Chem. Abs.*, 1933, **27**, 1012; *cf.* Dreyfus, French Patent 737,612, 1932; *Chem. Abs.*, 1933, **27**, 1638.

[39a] Soc. française de catalyse généralisée, French Patent 41,255, 1931; *Chem. Abs.*, 1933, **27**, 2163; addition to French Patent 729,952, 1931; *Chem. Abs.*, 1933, **27**, 312.

[40] U. S. Patent 1,875,310, Aug. 30, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, **26**, 5856.

[40a] See Wurtz, "Dictionnaire de chimie," Libraire Hachette et Cie., Paris, 2nd Supplement, 1907, **6**, 188.

[41] "International Critical Tables," National Research Council, McGraw-Hill Book Co., New York, 1926, **1**, 180. See also Lawrie, "Glycerol and the Glycols," Chemical Catalog Co., Inc., New York, 1928, 368.

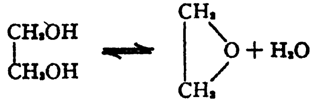
[42] Taylor and Rinkenbach, *Ind. Eng. Chem.*, 1926, **18**, 676.

[43] Curme and Young, *Chem. Met. Eng.*, 1923, **28**, 169.

[44] de Forcrand, *Compt. rend.*, 1901, **132**, 688; *Chem. Soc. Abs.*, 1901, **80** (1), 307.

[45] de Forcrand, *Ann. chim.*, 1890, **20**, 442; *Compt. rend.*, 1891, **113**, 1048; *ibid.*, 1892, **114**, 125, 301, 545; *Bull. soc. chim.*, 1892, (3) **7**, 23; also, Van Loon, U. S. Patent 1,681,600, Aug. 21, 1928; *Brit. Chem. Abs.* **B**, 1928, 886.

On dehydration, ethylene glycol yields ethylene oxide to some extent:

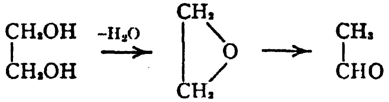


In this reaction, however, polyglycols are also produced depending upon the conditions. The formation of diethylene and triethylene glycols from ethylene glycol by elimination of water may be represented as follows:

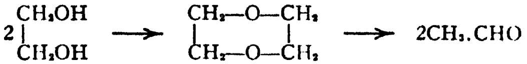
$$HOCH_2CH_2OH + HOCH_2CH_2OH \longrightarrow \underset{\textit{diethylene glycol}}{HOCH_2CH_2{-}O{-}CH_2CH_2OH} + H_2O$$

$$HOCH_2CH_2{-}O{-}CH_2CH_2OH + HOCH_2CH_2OH$$
$$\longrightarrow \underset{\textit{triethylene glycol}}{HOCH_2CH_2{-}O{-}CH_2CH_2{-}O{-}CH_2CH_2OH} + H_2O$$

In the presence of dilute mineral acids at fairly high temperatures (200° to 210° C.) ethylene glycol undergoes dehydration with the production of acetaldehyde, as well as other substances.[46] In this reaction Baeyer and Erlenmeyer[47] both assumed the intermediate formation of an unsaturated alcohol which was isomerized to acetaldehyde. Krassuski[48] believed that ethylene oxide was the intermediate compound thus:

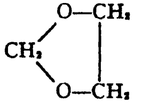


On the other hand, Favorsky,[49] by distilling glycol with 4 per cent concentrated sulphuric acid, obtained mainly dioxan with acetaldehyde and glycol acetal. Distillation of dioxan with dilute sulphuric acid was found to yield some acetaldehyde and acetal and, therefore, Favorsky assumed that the reaction proceeded through the intermediate formation of dioxan, thus:



In a similar way, propylene glycol when heated to 220° C. with very small amounts of hydrochloric acid, yielded propionaldehyde mainly.[50]

A considerable number of cyclic acetals (or cyclic diethers) of ethylene glycol are known. A methylal of ethylene glycol was prepared by Trillat and Cambier[51] by gently heating equimolecular quantities of trioxymethylene and ethylene glycol with 2 per cent ferric chloride. This substance, which was subsequently shown by Henry[52] to have the structure:



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[46] *Cf.* Nevole, *Bull. soc. chim.*, 1876, (2) 25, 289; *Chem. Soc. Abs.*, 1877, 31, 58.

[47] See Favorsky, *loc. cit.*

[48] *J. Russ. Phys. Chem. Soc.*, 1902, 34, 537; *Chem. Zentr.*, 1902, 2, 1095; *Chem. Soc. Abs.*, 1903, 84 (1), 8.

[49] *J. Russ. Phys. Chem. Soc.*, 1906, 38, 741; *Chem. Zentr.*, 1907, 1, 15; *Chem. Soc. Abs.*, 1907, 92 (1), 274.

[50] Linnemann, *Ann.*, 1878, 192, 61; *Chem. Soc. Abs.*, 1878, 34, 776.

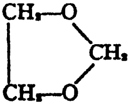
[51] *Compt. rend.*, 1894, 118, 1279; *Chem. Soc. Abs.*, 1894, 66 (1), 487.

[52] *Compt. rend.*, 1895, 120, 107; *Chem. Soc. Abs.*, 1895, 68 (1), 266.

is a liquid boiling at 74°-75° C. It can also be prepared by heating together 100 grams of glycol, 50 grams of 40 per cent formaldehyde solution, and 50 grams of syrupy phosphoric acid. In the same way, acetaldehyde and glycol yield an acetal boiling at 82° C. and isobutyraldehyde forms an acetal which boils at 122° C.[53] Cyclic diethers can be obtained by the reaction of glycols with an aqueous solution containing equimolecular quantities of water and an aldehyde or ketone in the presence of sulphuric acid at 140° C., according to Dreyfus.[53a]

Cyclic acetals are also obtainable by condensing glycol with butyraldehyde[54] and crotonaldehyde,[55] and also by condensing acetylene with glycol in the presence of mercuric sulphate.[56] In the latter, acetaldehyde is apparently the intermediate compound which immediately condenses with the glycol.

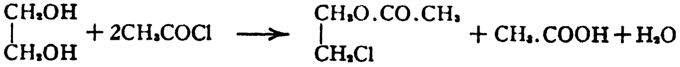
A method of producing cyclic ethers of glycols consists in the reaction of halogenated ethers with metallic oxides. Thus, the cyclic acetal,



may be prepared from chloromethyl-β-chloroethyl ether and copper oxide.[57] Various cyclic acetals obtained by condensing phenylated aliphatic aldehydes with 1,2-glycols are said to be usable in the preparation of perfumes. Among these may be mentioned the cyclic acetal from phenylacetaldehyde and ethylene glycol, which has a rose-like odor.[58]

The decomposition of ethylene glycol in the presence of vanadium pentoxide has been studied by Drake and Smith.[59] At 250° to 400° C. the main decomposition products are acetaldehyde and ethylene but small amounts of oxides of carbon and acetic acid are also formed. At temperatures up to about 320° C., ethylene is the major product. The minimum amount of ethylene results at about 360° C., at which temperature aldehyde formation is at a maximum.

Ethylene glycol, containing two hydroxyl groups, reacts with phosphorus pentachloride yielding ethylene dichloride.[60] With organic acid chlorides the 1,2-glycols react with the formation of acyl derivatives of the corresponding chlorohydrins.[61] In the case of ethylene glycol and acetyl chloride this reaction can be represented as:



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2CH_3COCl \longrightarrow \begin{matrix} CH_2O.CO.CH_3 \\ | \\ CH_2Cl \end{matrix} + CH_3.COOH + H_2O$$

On treatment with concentrated hydrochloric acid at 148° to 160° C. ethylene glycol is partly converted into the chlorohydrin,[62] but at 200° C. (or at lower temperatures in the presence of hydrogen chloride), ethylene dichloride is formed.[63]

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[53] Verley, *Bull. soc. chim.*, 1899, (3) 21, 275; *Chem. Soc. Abs.*, 1899, 76 (1), 665.

[53a] French Patents 745,973 and 745,974, 1933; *Chem. Abs.*, 1933, 27, 4243; *cf.* British Patent 393,608, 1931; *Brit. Chem. Abs.* **B**, 1933, 822.

[54] Leopold and Michael, German Patent 419,223, 1924; assigned to Farbenfabrik vorm. Meister, Lucius and Brüning; *Brit. Chem. Abs.* **B**, 1926, 248.

[55] I. G. Farbenindustrie A.-G., German Patent 434,989, 1926.

[56] Walter, U. S. Patent 1,669,384, May 8, 1928; British Patent 288,707, 1927; *Brit. Chem. Abs.* **B**, 1928, 440; both patents assigned to Verein für Chem. Ind. A.-G.

[57] Dreyfus, British Patent 374,134, 1931; *Brit. Chem. Abs.* **B**, 1932, 832; French Patent 729,416, 1932; *Chem. Abs.*, 1932, 26, 5964.

[58] I. G. Farbenindustrie A.-G., British Patent 346,115, 1930; *Brit. Chem. Abs.* **B**, 1931, 710.

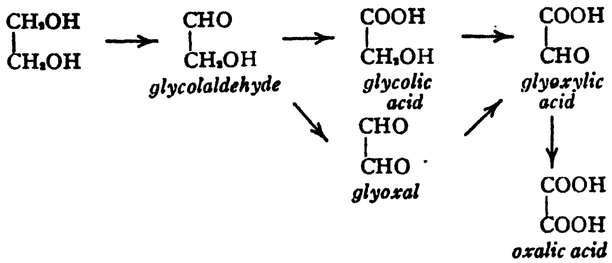
[59] *J.A.C.S.*, 1930, 52, 4558.

[60] Wurtz, *Ann. chim.*, 1859, (3) 55, 419.

[61] Lourenço, *Ann. chim.*, 1863, (3) 67, 254.

[62] Ladenburg, *Ber.*, 1883, 16, 1407.

On oxidation (with nitric acid or alkaline lead peroxide) ethylene glycol is converted into one or more products,[64] the various steps being represented as follows:



Because of its solvent action, which approximates that of ethyl alcohol for certain substances, ethylene glycol has found some application in the preparation of flavoring extracts. The toxicity of ethylene glycol toward dogs, rabbits, and rats was studied by Page[65] who compared its effects with those of glucose and glycerol. Injected intravenously, it quickly lowered the blood pressure. Tests on rabbits by Fuller[66] showed that 5 to 10 cc. doses administered daily in 50 per cent aqueous solution produced no pathological symptoms. Daily doses of 15 to 20 cc. in 50 per cent aqueous solution were attended with no outward symptoms but autopsies revealed evidence of chronic gastritis. Since these doses are, however, far in excess of what would be absorbed by a human being in a food product, Fuller concluded that ethylene glycol could be safely used in such materials.

Experiments on its inhibitory and disinfectant action toward *Bacillus typhosus* (Rawlings), a wine yeast and a mixed mold culture indicated that its value in this respect lies between that of glycerol and ethyl alcohol and does not fall far short of the latter. In direct opposition to Fuller's conclusions, Hunt[67] stated that ethylene glycol is as poisonous as methanol and that its toxicity is to be attributed to oxalic acid which is formed by oxidation in the body. Hunt's statements have been contested by Hanzlik[68] but, in reply, Hunt[69] cited additional evidence in support of his contention. The use of ethylene glycol in food products, according to Hunt, is to be deprecated, although there is no objection to its application in certain medicinal preparations. Two serious cases of ethylene glycol poisoning were reported by Brekke,[70] the initial symptoms being similar to alcohol intoxication, followed later by paralysis of some of the cerebral nerves and hemorrhagic nephritis. The irritant and toxic properties of ethylene glycol have been investigated by Hanzlik, Seidenfeld and Johnson,[71] and the relation between the pharmacological action and the chemical constitution of ethylene glycol derivatives have been discussed by von Oettingen and Jirouch.[72]

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[63] Schorlemmer, *J.C.S.*, 1881, **39**, 143.

[64] Wurtz, *Ann. chim.*, 1859, (3) **55**, 414, 417; Debus, *Ann.*, 1859, **110**, 319; Gläser and Morawski, *Monatsh.*, 1889, **10**, 582; Nef, *Ann.*, 1907, **357**, 292; Trillat, *Bull. soc. chim.*, 1903, (3) **29**, 35; *Chem. Zentr.*, 1903, **1**, 438.

[65] *J. Pharmacol.*, 1927, **30**, 313; *Chem. Abs.*, 1927, **21**, 1150.

[66] *Ind. Eng. Chem.*, 1924, **16**, 624.

[67] *Ind. Eng. Chem.*, 1932, **24**, 361.

[68] *Ind. Eng. Chem.*, 1932, **24**, 836.

[69] *Ind. Eng. Chem.*, 1932, **24**, 836.

[70] *Norsk. Mag. Laegev*, 1930, **91**, 381; *Chem. Abs.*, 1932, **26**, 772.

[71] *J. Pharm. Exp. Ther.*, 1931, **41**, 387; *Chem. Abs.*, 1931, **25**, 4938.

[72] *J. Pharm. Exp. Ther.*, 1931, **42**, 355; *Chem. Abs.*, 1932, **26**, 1033.

Applications of Ethylene Glycol

Ethylene glycol has found use in the preparation of glycol dinitrate, as an anti-freeze for automobile radiators, and as a solvent and preservative in food products and medicines. The properties and applications of glycol dinitrate are described later.

The use of ethylene glycol as an anti-freeze in automobile radiators is largely the result of efforts of the Carbide and Carbon Chemicals Corporation,[73] who marketed this material under the trade name of "Prestone". The specifications of an ideal anti-freeze solution, as drawn up by the U. S. Bureau of Standards,[74] are as follows:

The material shall prevent freezing of the radiator liquid without injuring engine or radiator. The non-freezing properties of the solution should, moreover, be permanent and not reduced on continued use. Furthermore, the material should not materially change the boiling point of water when dissolved in it.

To the above specifications, might advantageously be added: The material should be odorless, non-inflammable, non-corrosive, and should not attack automobile finishes and its aqueous solutions should possess a high heat capacity and a low vicosity.[75]

Of the other materials which have been proposed for anti-freeze solutions, ethyl alcohol and glycerol have found extensive application. Ethylene glycol fulfills the requirements of an anti-freeze. In aqueous solution it depresses the freezing point in proportion to the concentration present, down to about 60 per cent by volume, which solution freezes at —49° C. (—56° F.). For higher concentrations of glycol, the freezing point increases again to —11.6° C. (11.3° F.), that of pure glycol. The use of 1,2-glycols, particularly ethylene glycol, in aqueous solution as anti-freeze liquids in automobile cooling systems was described by Hibbert.[76] Mixtures containing 60 to 65 parts of water and 35 to 40 parts of 1,2-glycols are particularly satisfactory for this purpose.

As a solvent,[76a] ethylene glycol has many of the characteristics of ethyl alcohol. It dissolves esters, medicaments, resins, flavors, and dyes. The use of ethylene glycol as a solvent in the manufacture of concentrated fruit flavors, flavoring extracts and similar commodities has been discussed by Fuller[77] and Smith and Eoff.[78]

The combined preservative and hygroscopic nature of ethylene glycol recommend it for a wide variety of applications, especially in the manufacture of cosmetics, in the preparation of anatomical and biological specimens, in the treatment of skin and furs, in the moistening of tobacco, as a means of preserving the suppleness and flexibility of leather during processing, and in the textile industry as an aid to the finishing and dyeing of fabrics.[79] According to McElroy[80] a good hygroscopic composition for incorporation in medicinal products consists of ethylene glycol, water, and a water-soluble substance such as cane sugar, invert sugar, lactose, calcium chloride or boric acid.

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[73] See Curme and Young, *Chem. Met. Eng.*, 1923, 28, 169.

[74] *Bur. Standards, Letter Circular*, 28 (Dec., 1921).

[75] Curme and Young, *Ind. Eng. Chem.*, 1925, 17, 1117.

[76] U. S. Patent 1,213,368, Jan. 23, 1917; *Chem. Abs.*, 1917, 11, 877. See also Curme and Young, *Chem. Met. Eng.*, 1923, 28, 169; *Chem. Abs.*, 1923, 17, 1427; *Ind. Eng. Chem.*, 1925, 17, 1117; Killeffer, *Ind. Eng. Chem.*, 1926, 18, 1043; Keyes, *Ind. Eng. Chem.*, 1927, 19, 1119; Anon., *Science*, Nov. 19, 1926, Suppl., 14.

[76a] The production and uses of solvents were reviewed by Reid, *Ind. Eng. Chem.*, 1934, 26, 21.

[77] *Ind. Eng. Chem.*, 1924, 16, 624.

[78] U. S. Patent 1,384,681, July 12, 1921; *Chem. Abs.*, 1921, 15, 3696.

[79] Curme and Young, *Chem. Met. Eng.*, 1923, 28, 169.

[80] U. S. Patent 1,268,135, June 4, 1918; assigned to Chemical Development Co.; *Chem. Abs.*, 1918, 12, 1819.

The use of ethylene glycol as a substitute for glycerol in some of its applications has been described by Braun[81] and its employment in the grading of collodion membranes has been investigated by Field and Thomas.[82]

Numerous derivatives of ethylene glycol, such as esters and ethers, are finding important applications in the chemical industry. With the exception of the dinitrate, most of these materials are being manufactured from either the olefin dichloride or the chlorohydrin. Synthetic resins have been produced, for example, by condensation of ethylene glycol with phthalic anhydride.[83] Ethylene glycol has been used in liquid media for heat-transfer[84] and as an absorption liquid for methylamine in refrigeration.[85] In the manufacture of beeswax candles,[86] sticking to the molds is said to be prevented by the incorporation of 5 per cent of the glycol. A selective solvent prepared by mixing a glycol with phenol has been proposed by Stratford[86a] for removing impurities from kerosene or lubricating oils. Thomas and Hochwalt[86b] used a solution of sodium potassium carbonate in ethylene glycol and water as an anti-freeze charge for carbonate-sulphuric acid fire extinguishers. Reddish blue dyestuffs have been obtained by condensing ethylene glycol with halogenated dibenzanthrones, containing at least two halogen atoms.[87]

ETHYLENE GLYCOL DINITRATE

Henry[88] was the first to prepare and identify glycol dinitrate. This compound was made by dropping small portions of the glycol into a mixture of sulphuric and nitric acids cooled to 0° C. Previously, however, Kekulé[89] had obtained a mixture of the glycol dinitrate and the nitric ester of β-nitroethanol[90] ($CH_2(O.NO_2)CH_2NO_2$) by the nitration of ethylene. Champion[91] prepared the dinitrate by solution of 42 grams of glycol in a mixture of 100 grams of fuming nitric acid and 200 grams of 66° Bé sulphuric acid, and Nef[92] used 10 cc. of the glycol with a mixture of 20 cc. of nitric acid (specific gravity, 1.52) and 40 cc. of sulphuric acid (specific gravity, 1.8), cooled to —10° to —15° C. The method employed by Rinkenbach[93] consisted in slowly adding 20 grams of purified glycol[94] to a mixture of 70 grams of nitric acid (specific gravity, 1.42) and 130 grams of sulphuric acid (specific gravity, 1.84) at a temperature of

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[81] *Am. Perfumer,* 1928, **23**, 513; *Chem. Abs.*, 1929, **23**, 1613.

[82] *Proc. Soc. Exptl. Biol. Med.*, 1928, **25**, 679; *Chem. Abs.*, 1928, **22**, 4553.

[83] E.g., Callahan, U. S. Patent 1,108,329, Aug. 25, 1914; assigned to General Electric Co.; *Chem. Abs.*, 1914, **8**, 3506; Ellis, U. S. Patents 1,843,870, Feb. 2, 1932; *Chem. Abs.*, 1932, **26**, 1812; 1,876,886, Sept. 13, 1932; 1,886,242, Nov. 1, 1932; 1,897,977, Feb. 17, 1933; Bradley, U. S. Patents 1,923,704 and 1,923,715, Aug. 22, 1933; Ellis, U. S. Patent 1,923,714, Aug. 22, 1933; all assigned to Ellis-Foster Company. Kienle and Hovey, *J.A.C.S.*, 1930, **52**, 3636. See also Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York.

[84] Sherman, U. S. Patent 1,805,500, May 19, 1931; assigned to Gen. Frigheatone Co., Inc.; *Brit. Chem. Abs.* **B**, 1932, 84; Moormann, U. S. Patent 1,820,085, Aug. 25, 1931; assigned to Shaler Co.; *Brit. Chem. Abs.* **B**, 1932, 485.

[85] Platen-Munters Refrigerating System Aktiebolag, German Patent 531,218, 1929; *Chem. Abs.*, 1931, **25**, 5481. Tandberg (British Patent 329,790, 1929; assigned to Electrolux, Ltd.; *Chem. Abs.*, 1930, **24**, 5899) gives some further details for the use of ethylene glycol as an absorbent in refrigerating systems.

[86] Geller, U. S. Patent 1,866,025, July 5, 1932; assigned to Will and Baumer Candle Co.; *Chem. Abs.*, 1932, **26**, 4494.

[86a] U. S. Patent 1,892,655, Dec. 27, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 2291. Clark and Harding (U. S. Patent 1,776,550, Sept. 23, 1930; *Brit. Chem. Abs.* **B**, 1931, 578) used a polyhydric alcohol to extract unsaturated substances from lubricating or insulating oils.

[86b] U. S. Patent 1,777,339, Oct. 7, 1930; *Brit. Chem. Abs.* **B**, 1931, 522.

[87] Thomson and Thomas, U. S. Patent 1,818,510, Aug. 11, 1931; assigned to Scottish Dyes, Ltd.; *Chem. Abs.*, 1931, **25**, 5577.

[88] *Ber.*, 1870, **3**, 529; *Ann. chim. phys.*, 1872, (4) **27**, 243.

[89] *Ber.*, 1869, **2**, 329.

[90] See Wieland and Sakellarios, *Ber.*, 1920, **53**, 201.

[91] *Compt. rend.*, 1871, **73**, 571; *Chem. Zentr.*, 1871, 611; *Z. für Chem.*, 1871, 469.

[92] *Ann.*, 1899, **309**, 126.

[93] *Ind. Eng. Chem.*, 1926, **18**, 1195.

[94] Purified by method of Taylor and Rinkenbach, *Ind. Eng. Chem.*, 1926, **18**, 676.

23° C. The crude dinitrate (49 grams) separated and after washing with 300 cc. of water in small portions, a yield of 39.6 grams of acid-free material resulted. The low yield can be improved by maintaining a lower temperature and by using a different nitrating acid mixture. The product obtained possessed a nitrogen content of 18.37 per cent (theoretical, 18.43 per cent).

According to Rinkenbach, pure ethylene glycol dinitrate is a colorless, neutral, mobile liquid at ordinary temperatures, with a peculiar sweetish taste and no appreciable odor. Its physical properties are as follows: D^{0}_{15} 1.5176; D^{15}_{15} 1.4962; D^{25}_{15} 1.4817; freezing point, —22.3° C.; heat of fusion, 30.0 cal. per g.; heat of combustion, 268.22 kg.-cal. (constant volume) or 266.48 kg.-cal. (constant pressure) per mole; n^{0}_{D} 1.4546; n^{15}_{D} 1.4491; n^{30}_{D} 1.4436; heat of formation, 365.5 cal. per g.; vapor pressure at 0° C., 0.0072 mm. and at 22° C., 0.0565 mm. (Rinkenbach) or 0.0465 mm. (Crater[95]).

Various other methods for the preparation of the dinitrate alone or in admixture for use in explosives have also been devised.[96] Among these are procedures which deal with the production of the dinitrate by nitration of glycol or ethylene oxide,[97] of sulphoglycol,[98] of mixtures of glycols,[99] of ethylene,[100] and of the condensation products of glycol with 3,4-dinitrochlorobenzene.[101] Hough[102] proposed to mix the dinitrate with nitroglycerol and Matthews, Strange and Bliss[103] described explosives containing nitrated 1,2-glycols, nitroglycerol and infusorial earth. Explosives containing nitroglycerol with nitrocellulose and nitrate salts[104] are said to have been manufactured industrially in Europe.[105] Several explosives containing nitrated 1,2-glycols were suggested by Barab,[106] who has also recommended propylene glycol dinitrate[107] for this purpose.

The great value of glycol dinitrates in explosives lies in their low freezing point and their capacity to form low freezing mixtures with nitroglycerol. They possess lower sensitivity to shock and greater fluidity than nitroglycerol, together with perfect oxygen balance and they are practically non-hygroscopic. About 9 million pounds of ethylene glycol were employed in the manufacture of low-freezing dynamites in the United States in 1927.[108]

The physiological action of glycol dinitrate is similar to that of nitroglycerol but because of its higher vapor pressure (approximately 150 times greater than that of glyceryl trinitrate at 22° C.) the inhalation of sufficient vapor to cause injurious effects is more likely to occur. This high volatility is one objection to the use of glycol dinitrates.[109] Because of the toxicity of the volatile dinitrate, Schmid[110] recommended a continuous nitration process for its manufacture. Gelatinization of nitrocotton is effected more quickly by glycol dinitrate than by nitroglycerol so that a slow-gelatinizing nitrocotton must be used, or uneven results are obtained. Homogeneous transparent "gelatins" were prepared by Schmid by gelatinization at 0° to 1.5° C. Compared with the gelatins obtained from nitroglycerol, those from glycol dinitrate are stickier and not so stiff, but this disadvantage is overcome by the use of larger amounts of nitrocotton and absorbent.

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[95] *Ind. Eng. Chem.*, 1929, **21**, 674.

[96] Claessen, German Patent 179,789, 1904; *Chem. Zentr.*, 1907, **1**, 1475.

[97] Matthews and Strange, British Patent 12,770, 1912; *Chem. Abs.*, 1913, **7**, 3842.

[98] Jolicard, French Patent 456,456, 1912; *Chem. Abs.*, 1914, **8**, 1872.

[99] Hibbert, U. S. Patents 1,213,367 and 1,213,369, Jan. 23, 1917; *Chem. Abs.*, 1917, **11**, 888; U. S. Patent 1,231,351, June 26, 1917; *Chem. Abs.*, 1917, **11**, 2407.

[100] Oehme, German Patent 338,056, 1918; *J.S.C.I.*, 1921, **40**, 640A; U. S. Patent 1,426,313, Aug. 15, 1922; *Chem. Abs.*, 1922, **16**, 3316.

[101] Lewis, U. S. Patent 1,560,426, Nov. 3, 1925; *Chem. Abs.*, 1926, **20**, 112.

[102] U. S. Patent 1,206,233, Nov. 28, 1916; *Chem. Abs.*, 1917, **11**, 211.

[103] French Patent 458,309, 1913; *Chem. Abs.*, 1914, **8**, 2807.

[104] Jolicard. French Patent 456,456, 1912; *loc. cit.*

[105] Brooks, *Chem. Met. Eng.*, 1920, **22**, 631.

[106] U. S. Patents 1,307,032, 1,307,033 and 1,307,034, June 17, 1919; *Chem. Abs.*, 1919, **13**, 2281, 2282.

[107] U. S. Patent 1,371,215, Mar. 15, 1921; *Chem. Abs.*, 1921, **15**, 1815.

[108] *J.S.C.I.*, 1928, **47**, 1270.

[109] See Rinkenbach, *Ind. Eng. Chem.*, 1926, **18**, 1195; *Chem. Met. Eng.*, 1927, **34**, 296; Brooks, *loc. cit.*; Curme and Young, *Chem. Met. Eng.*, 1923, **28**, 169.

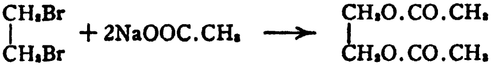
[110] *Z. Ges. Schliess- u. Sprengstoffw.*, 1927, **22**, 273; *Brit. Chem. Abs.* **B**, 1927, 926.

ETHYLENE GLYCOL ACETATES

Both mono- and di-esters of the glycols are known, the methods for their technical production being:

(1) Reaction of ethylene dihalide (especially dichloride) with salts of fatty acids.
(2) Esterification of glycols with fatty acids or their anhydrides.
(3) Condensation of olefin oxides with fatty acids or their anhydrides.

The reaction of ethylene dihalides with salts of organic acids appears to be a fairly general method for the preparation of glycol esters. Depending upon the relative proportions of the reactants, either the mono- or di-esters may be formed. Thus, Atkinson[111] obtained glycol monoacetate by heating the dibromide with potassium acetate in 85 per cent alcohol. Henry[112] heated 570 grams of ethylene dibromide and 300 grams of anhydrous potassium acetate with the addition of a little acetic anhydride for 10 hours and obtained an almost quantitative yield of the diacetate:



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2NaOOC.CH_3 \longrightarrow \begin{matrix} CH_2O.CO.CH_3 \\ | \\ CH_2O.CO.CH_3 \end{matrix}$$

Drushel and Bancroft[113] boiled 300 grams of the dibromide with 155 grams of fused potassium acetate in 300 grams of 85 per cent alcohol for 18 hours and obtained 83 grams of diacetate, but no monoacetate.

From a technical standpoint, it is far too expensive to employ bromides and potassium salts for the production of glycol esters. Good results have been achieved with ethylene dichloride and the sodium salts of organic acids. For example, glycol diacetate may be readily prepared from ethylene dichloride and anhydrous sodium acetate.[114] According to Rodebush,[115] glycol esters are made by heating a mixture of ethylene dichloride, fused potassium, sodium, calcium, or magnesium acetates, and alcohol to 180° C. under pressure for 1 hour. The method is applicable to the preparation of numerous esters of ethylene glycol, including the salicylate[116] and stearate.[117] The commercial preparation of glycol diacetate is described as follows by Killeffer.[118] One mole of ethylene dichloride, slightly more than two moles of anhydrous sodium acetate (or better, 5 per cent in excess of this) and 2 to 3 per cent of glycol diacetate, are mixed, stirred, and heated in an autoclave at pressures of 125 to 150 pounds per square inch until the pressure drops, indicating that all the volatile dichloride is consumed. The product is then distilled off.

The second general method of preparation of glycol esters was employed by

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[111] *Ann.*, 1859, 109, 232; *Phil. Mag.*, 1859, 66, 433; see also Demole, *Ber.*, 1874, 7, 70, 641; *Chem. Soc. Abs.*, 1874, 27, 783; *Ann.*, 1874, 173, 117; *ibid.*, 1875, 177, 49.

[112] *Rec. trav. chim.*, 1901, 20, 243; *Chem. Soc. Abs.*, 1901, 80 (1), 577; *Bull. acad. roy. Belg.*, 1906, 30, 732; *Chem. Soc. Abs.*, 1907, 92 (1), 377; also Seelig, German Patent 41,507, 1887; *Chem. Zentr.*, 1888, 88.

[113] *Am. J. Science*, 1917, 44, 371; *Chem. Abs.*, 1918, 12, 148.

[114] Meyer, German Patent 332,677, 1919; *J.S.C.I.*, 1921, 40, 370A; Engelhardt, German Patent 404,999, 1919; assigned to Farbenfabriken vorm. F. Bayer and Co.; *J.S.C.I.*, 1925, 44, 425B.

[115] U. S. Patent 1,430,324, Sept. 26, 1922; *Chem. Abs.*, 1922, 16, 3903.

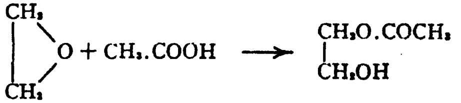
[116] C. F. Boehringer und Söhne, German Patent 218,466, 1907; *Chem. Zentr.*, 1910, 1, 782.

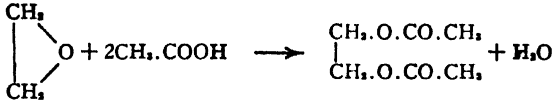
[117] Ayres and Haabestad, Canadian Patent 286,077, 1929; assigned to B. A. S. Co.; *Chem. Abs.*, 1929, 23, 1417.

[118] *Ind. Eng. Chem.*, 1927, 19, 636.

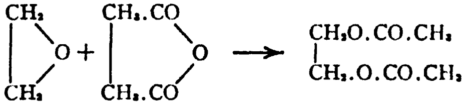
Drushel and Bancroft[119] to make the monoacetate of ethylene glycol by heating equimolecular quantities of glacial acetic acid and the glycol with anhydrous copper sulphate. According to Watson,[120] either the mono- or di-esters of the glycols may be obtained, depending upon the proportions of the reactants. To obviate the use of catalysts, such as sulphuric acid, which promote undesirable side reactions, the water formed in the reaction can be removed by continuous distillation during the esterification. In making ethylene glycol monoacetate, for example, commercial glycol is refluxed with a little more than the stoichiometric quantity of commercial 28 per cent acetic acid, allowing water vapors to escape and returning acid and glycol back to the reaction mixture. When the acidity has been reduced to the extent required, the residual acid is distilled off and the crude ester fractionated. In the production of the diacetate, the procedure is the same except, of course, that twice the quantity of acid is added. The process is applicable to the production of di- and mono-formates, valerates, oleates, stearates, and other esters.

The third method for making esters of glycols consists in the condensation of an olefin oxide with an anhydrous organic acid, often in the presence of a condensing agent. By this method, Wurtz[121] obtained both the mono- and diacetates of ethylene glycol according to the reactions:





Condensation of ethylene oxide with glacial acetic acid yields a mixture of the mono- and di-acetates, and it has been observed that anhydrous ferric chloride facilitates the esterification.[122] On the other hand, condensation of ethylene oxide with acetic anhydride (or other acid anhydrides) yields the di-ester exclusively:



Inorganic acids (sulphuric acid) or an acid salt (sodium bisulphate) or a salt of a strong base with an organic acid other than that to be esterified, have been suggested for condensing olefin oxides with organic acids.[123] In another process[124] the reaction between alkylene oxides and carboxylic acids is catalyzed by an acidulated aluminum hydrosilicate in which the hydrogen-ion concentration produced by suspension of the catalyst in water corresponds to a p_H value of less than 3.

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[119] *Loc. cit.*

[120] U. S. Patent 1,534,752, Apr. 21, 1925; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1925, **19**, 1710.

[121] *Loc. cit.*

[122] Arndt, Eistert, and Ender, *Ber.*, 1929, **62**, 44.

[123] I. G. Farbenindustrie A.-G., British Patent 292,059, 1927; *Chem. Abs.*, 1929, **23**, 1417.

[124] I. G. Farbenindustrie A.-G., French Patent 39,773, 1931; addition to French Patent 610,282, 1926; *Brit. Chem. Abs.* **B**, 1927, 348; *Chem. Abs.*, 1932, **26**, 4826.

Ethylene glycol monoacetate (boiling point, 181° C.) can be used as a solvent, especially for various synthetic resins derived from urea-formaldehyde condensations.[125] On account of the presence of a free hydroxyl group it is a water-soluble solvent. Ethylene glycol diacetate (boiling point, 186° C.) is a solvent for both cellulose acetate and nitrate as well as for certain resins. It possesses a slight odor similar to that of ethyl acetate, but rather less pronounced, and has been suggested as a solvent for flavors and as a fixative in perfumery.[126] Glycol monoacetate is said to be a satisfactory solvent for the deresination of crude montan wax.[127] Both the mono- and di-acetates can be used for removing free fatty acids from oils or fats.[128]

Many other mono- and di-esters of ethylene glycol are known but they do not appear to be of industrial importance. Ethylene glycol monobenzoate is a solid melting at 45° C., which can be dissolved in almost any proportions in solutions of the alkali salts of benzoic, toluic, and salicylic acids.[129] The monochloroacetic ester of ethylene glycol has been proposed as a denaturant for alcohol.[130] The glycol diester of monochloroacetic acid has been recommended as an insecticide, fungicide and disinfectant when diluted with kerosene.[131]

GLYCOL ESTERS OF DICARBOXYLIC ACIDS

The esters of the glycols with dibasic acids polymerize readily, very few of them being known in the monomeric condition.[132] Monomeric ethylene glycol oxalate is a crystalline solid (melting point, 143° C.) which, on standing for a few days in a stoppered bottle, is spontaneously transformed into a powder consisting of a mixture of polymers. By extraction with cold solvents this polymerized product can be separated into two fractions, one melting at 159° C. and having an apparent molecular weight of about 3000, and another melting at 173° C., which probably has a much higher molecular weight. These fractions, on standing, are still further converted, part of them going to the monomer.

When ethylene glycol is heated with an equimolecular proportion of succinic, adipic, phthalic, or other dibasic acid, the products are highly polymerized esters. These polymerized esters are non-volatile, dissolve quite readily in cold chloroform, and probably consist of a mixture of substances of varying molecular weights. Despite their high molecular weights and lack of homogeneity, with the exception of the phthalates, they are micro-crystalline solids. The chemical constitution of these substances has been elucidated by Carothers and his co-workers, who have shown that they are open-chain molecules containing alternate links of glycol and acid radicals. Thus, the neutral glycol succinates possess the structure:

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[125] Killeffer, *Ind. Eng. Chem.*, 1927, **19**, 636; see also Tilicheyev, *J. Russ. Phys.-Chem. Soc.*, 1927, **58**, 447; *Chem. Abs.*, 1927, **21**, 3358.

[126] Killeffer, *loc. cit.*

[127] Pungs and Freytag, German Patent 523,531, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3812.

[128] Franzen and Schellmann, German Patent 526,492, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 4427.

[129] Farbenfabriken vorm. F. Bayer and Co., German Patent 298,185, 1915.

[130] Fuller, U. S. Patent 1,573,698, Feb. 16, 1926; assigned to Union Carbide and Carbon Research Laboratories; *Brit. Chem. Abs.* **B**, 1926, 337.

[131] Peet, U. S. Patent 1,816,441, July 28, 1931; assigned to Röhm and Haas Co.; *Chem. Abs.*, 1931, **25**, 5501.

[132] Lourenco. *Ann. chim. phys.*, 1863, **67**, 293; Davidoff, *Ber.*, 1886, **19**, 406; Vörlander, *Ann.*, 1894, **280**, 167; Tilicheyev, *J. Russ. Phys.-Chem. Soc.*, 1925, **57**, 143; *loc. cit.*; Carothers and Arvin, *J.A.C.S.*, 1929, **51**, 2560; Carothers and Van Natta, *J.A.C.S.*, 1930, **52**, 314; Carothers and Dorough, *J.A.C.S.*, 1930, **52**, 711; Carothers, Arvin and Dorough, *J.A.C.S.*, 1930, **52**, 3292; Carothers, *Chem. Reviews*, 1931, **8**, 361.

$$HO{-}[CH_2.CH_2.O.CO.CH_2.CH_2.CO.O]_x{-}CH_2.CH_2OH$$

in which X may be as high as 22.

Besides the above neutral polyesters, acidic polyesters may also be prepared by esterifying the glycol with an excess of the dibasic acid. A number of acidic ethylene glycol succinates, with molecular weights varying from about 1000 to 3000, have been thus prepared.

A highly viscous, colorless liquid, soluble in water, is obtained by heating equimolecular proportions of ethylene oxide and powdered phthalic acid at 60° to 65° C.[133] The yield is 180 per cent of the weight of phthalic acid.

GLYCOL ETHERS

Both mono- and di-alkyl ethers of ethylene glycol are known, the former being by far the more important industrially. The monoalkyl ethers form esters with organic acids. Both the monoalkyl ethers and their esters are solvents. The monoalkyl derivatives of ethylene glycol may be produced industrially in several ways.

Monoalkyl derivatives can be prepared by reaction of an olefin oxide with an alcohol or a phenol, usually in the presence of a catalyst. For this purpose, sulphuric acid has been proposed.[134] Thus, by passing ethylene oxide slowly into methyl alcohol containing 1 per cent of sulphuric acid at 15° C., a 90 per cent yield of the monomethyl ether is produced. The monoethyl ether can be prepared similarly. Young [135] employed higher temperatures and pressures, rather than catalysts, to effect this reaction. For example, a mixture of ethylene oxide and ethyl alcohol heated in an autoclave at 150° C. for 12 hours (or at 200° C. for 3 to 4 hours) gave a 70 per cent yield of the monoethyl ether.

Gibson and Payman [136] proposed to manufacture glycol monoalkyl ethers by condensing ethylene oxide with an alcohol in the presence of normal sulphates of multivalent elements, such as nickel, zinc, or chromium. On heating 82 parts of ethylene oxide, 410 parts of methyl alcohol and 2 parts of zinc sulphate in an autoclave at 100° to 105° C. for 6 to 8 hours, 102 parts (75 per cent) of the monomethyl ether formed. Similarly, by heating 88 parts of ethylene oxide with 440 parts of ethyl alcohol and 2 parts of nickel sulphate in an autoclave at 100° C., 126 parts of the monoethyl ether were obtained, a yield of 70 per cent of the theoretical.

Primary, secondary, and tertiary alcohols may be converted into their hydroxyalkyl ethers by reaction with olefin oxides in the presence of catalysts consisting of acidulated hydrosilicates, especially those of aluminum.[137] The hydrosilicates are activated by a preliminary acid treatment with an aqueous solution of a strong acid so that the resulting material, when dispersed in water, has a $p_{\rm H}$ value between 1.5 and 3.0. A stream of ethylene oxide (98.6 parts), for example, introduced into a mixture of 500 parts of ethyl alcohol and 25 parts of "Tonsil AC" (with a p_H value in water of 2.3) at 79° to 82° C., produced ethylene glycol monoethyl ether in yields of over 80 per cent (calculated on the ethylene oxide used). In a similar way, ethylene glycol monomethyl ether (85 per cent yield) can be prepared from ethylene oxide and methanol; 1,2-propylene glycol monoethyl ether (85 per cent yield), from 1,2-propylene oxide and ethyl alcohol; and butylene glycol monoethyl ether, from butylene oxides and ethyl alcohol.

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[133] Webel, German Patent 542,617, 1932; *Chem. Abs.*, 1932, **26**, 3264; German Patent 544,288, 1928; *Chem. Abs.*, 1932, **26**, 3518; both patents assigned to I. G. Farbenindustrie A.-G.

[134] I. G. Farbenindustrie A.-G., French Patent 610,282, 1926; *Brit. Chem. Abs.* **B**, 1927, 348; British Patent 271,169, 1926; *Chem. Abs.*, 1928, **22**, 1596.

[135] U. S. Patent 1,696,874, Dec. 25, 1928; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1929, **23**, 846.

[136] British Patent 322,037, 1928; *Chem. Abs.*, 1930, **24**, 2756; French Patent 684,126, 1930; U. S. Patent 1,774,089, Aug. 26, 1930; *Chem. Abs.*, 1930, **24**, 5043; patents assigned to Imperial Chemical Industries, Ltd.

[137] I. G. Farbenindustrie A.-G., British Patent 354,357, 1930; *Brit. Chem. Abs.* **B**, 1932, 12. The use of this catalyst for the reaction between alkylene oxides and organic acids has been mentioned in a preceding section.

A continuous process for the manufacture of glycol monoethers has been proposed,[138] in which a mixture of an olefin oxide and an organic hydroxy compound (in excess) is led continuously through a reaction vessel where the mixture is immediately heated to a temperature above 130° C., generally under pressures above 10 atmospheres. The advantages of such a process, in which catalysts are not employed, include rapid reaction with high production capacity, utilization of a considerable part of the heat of reaction to preheat fresh material, and development of relatively small pressures as a result of dilution of the volatile oxide by larger quantities of the second reactant. In practice, a mixture of 1 mole of ethylene oxide and 2 moles of ethyl alcohol is continuously pumped into a tower in which the liquid is immediately heated to 180° C., a pressure of 30 atmospheres being attained. The resulting solution is continuously fed to an open still, in which the solution is freed from excess alcohol. A theoretical yield of ethylene glycol monoethyl ether is said to be thus obtained. Similarly, an 85 per cent yield of ethylene glycol monophenyl ether may be produced by continuously pumping a mixture of 1 mole of ethylene oxide and 2 moles of phenol through a tower in which the mixture is rapidly heated to 200° C., the pressure developed being about 10 atmospheres.

In the process of Birch and Scott,[139] monoalkyl ethers of 1,2-glycols are produced by heating olefin oxides with alcohols under pressure in the presence of diethyl or dimethyl sulphate. Ethylene glycol monoethyl ether was formed in 90 to 95 per cent yield by heating ethylene oxide (30 volumes) and ethyl alcohol (300 volumes) at 100° C. under a pressure of 50 to 60 pounds per square inch with addition of a small amount (1 volume) of diethyl sulphate.

The condensation of alkylene oxides with hydroxy compounds is not limited to the simple monohydric alcohols, but may be applied to polyhydroxy compounds such as carbohydrates or polyvinyl alcohol.[140] Combination can be effected in alkaline aqueous media, even at room temperature, and the products are hydroxyalkyl ethers. For example, a polyvinyl alcohol treated with an olefin oxide, under pressure and in the presence of a basic catalyst (dimethylaniline or caustic soda, for example) yields water-soluble resinous hydroxyalkyl compounds which have been recommended for use as plastics, thickeners, and dressing and sizing agents.[141] Triethanolamine or other tertiary hydroxyalkylamines may also be condensed with olefin oxides to furnish more complex hydroxyalkyl ethers.[142]

A second important method for the production of monoalkyl ethers consists in treating either a glycol[143] or a chlorohydrin[144] with a dialkyl sulphate in the presence of caustic soda. The reactions in the case of ethylene glycol and chlorohydrin, condensed with diethyl sulphate to yield the monoethyl ether, are as follows:

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[138] I. G. Farbenindustrie A.-G., British Patent 342,022, 1929; *Brit. Chem. Abs.* **B**, 1931, 433.

[139] British Patent 367,353, 1932; assigned to Anglo-Persian Oil Co. Ltd.; *Brit. Chem. Abs.* **B**, 1932, 591; also French Patent 725,245, 1931; *Chem. Abs.*, 1932, **26**, 4825.

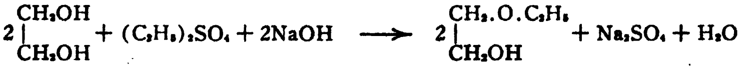
[140] Hagedorn, Ziese, Reyle and Bauer, U. S. Patent 1.876,920, Sept. 13, 1932; *Chem. Abs.*, 1933, **27**, 101; British Patent 368,530, 1931; *Brit. Chem. Abs.* **B**, 1932, 591; French Patent 713,427, 1931; *Chem. Abs.*, 1932, **26**, 1616; patents assigned to I. G. Farbenindustrie A.-G.

[141] I. G. Farbenindustrie A.-G., British Patent 364,323, 1930; *Brit. Chem. Abs.* **B**, 1932, 495.

[142] I. G. Farbenindustrie A.-G., British Patents 364,000 and 364,104, 1930; *Brit. Chem. Abs.* **B**, 1932, 495.

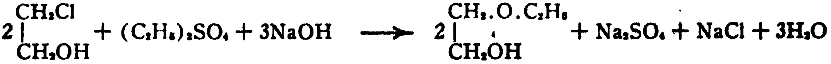
[143] Davidson, U. S. Patent 1,614,883, Jan. 18, 1927; assigned to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1927, 237.

[144] Davidson, U. S. Patent 1,732,356, Oct. 22, 1929; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1930, **24**, 127.



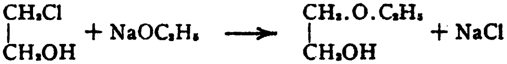
$$2\,\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} + (C_2H_5)_2SO_4 + 2NaOH \longrightarrow 2\,\begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2OH\end{array} + Na_2SO_4 + H_2O$$

and



$$2\,\begin{array}{l}CH_2Cl\\|\\CH_2OH\end{array} + (C_2H_5)_2SO_4 + 3NaOH \longrightarrow 2\,\begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2OH\end{array} + Na_2SO_4 + NaCl + 3H_2O$$

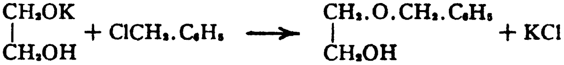
Another method of making monoalkyl ethers of the glycols consists in condensing an olefin oxide or a chlorohydrin with a sodium alcoholate. The reaction, with ethylene chlorohydrin, may be represented thus:



$$\begin{array}{l}CH_2Cl\\|\\CH_2OH\end{array} + NaOC_2H_5 \longrightarrow \begin{array}{l}CH_2.O.C_2H_5\\|\\CH_2OH\end{array} + NaCl$$

By this method, Cretcher and Pittenger[145] prepared the monoisopropyl, mono-n-propyl, monoisobutyl and monoamyl ethers of ethylene glycol. Similarly, ethylene glycol monobenzyl ether may be prepared from ethylene chlorohydrin and sodium benzylate.[146]

It is also possible to effect the synthesis by condensing a monopotassium derivative of a glycol with an alkyl chloride, e.g., the monopotassium salt of glycol condenses with benzyl chloride to form the monobenzyl ether (b.p., 132°-135° C. at 15 mm.):[146]



$$\begin{array}{l}CH_2OK\\|\\CH_2OH\end{array} + ClCH_2.C_6H_5 \longrightarrow \begin{array}{l}CH_2.O.CH_2.C_6H_5\\|\\CH_2OH\end{array} + KCl$$

Properties of Monoalkyl Ethers of Ethylene Glycol

The monoalkyl ethers of ethylene glycol are colorless, mobile liquids with practically no odor. They are solvents for cellulose nitrate, and the methyl ethers of the lower 1,2-glycols are also solvents for cellulose acetate. In general, they dissolve resins, oils and gums, the solubility of these materials increasing somewhat with increase in boiling point of the ether. Although the lower ethers are soluble in water, the butyl and isobutyl ethers of ethylene glycol have both upper and lower consolute temperatures.[147] The butyl ether of ethylene glycol is completely miscible with water above about 128° and below about 49° and similarly, the isobutyl ether, above about 150° and below about 25° C. The ethers are completely miscible with most organic solvents. The monoethyl ether is a powerful solvent for nitrocellulose, and resists dilution with non-solvents better than butyl acetate.[148] Table 105 summarizes some of the physical properties of the lower monoalkyl ethers of ethylene glycol.

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[145] *J.A.C.S.*, 1924, 46, 1503.

[146] Kayser and Schranz, U. S. Patent 1,651,458, Dec. 6, 1927; assigned to Winthrop Chemical Co.; *Chem. Abs.*, 1928, 22, 845.

[147] Cox and Cretcher, *J.A.C.S.*, 1926, 48, 451.

[148] Davidson, *Ind. Eng. Chem.*, 1926, 18, 669.

TABLE 105.—*Monoalkyl Ethers of Ethylene Glycol.*

	Boiling Point, ° C. at 743 mm.	D_{15}^{15}	n_D^{20}
Methyl	124.5	0.9748	1.4004
Ethyl	134.8	0.9360	1.4042
Isopropyl	144.0	0.9139	1.4080
n-Propyl	150.0	0.9110	1.4125
Isobutyl	158.8	0.9130	1.4135
n-Butyl	170.6	0.9188	1.4177
Isoamyl	181.0	0.9000	1.4198

The monoalkyl ethers of ethylene glycol have been proposed as solvents for cellulose acetate and nitrate in the lacquer industry[149] and also for use in anti-freeze solutions for automobile cooling systems.[150]

Ethylene glycol monomethyl ether is a solvent for cellulose esters and is specially adapted to the preparation of lacquers.[151] The carbonates of this and other ethers have been prepared by Drake and Carter.[152] The acetic acid ester of this monomethyl ether is a solvent for both cellulose acetate and nitrate and is miscible with water in all proportions.

Ethylene glycol monoethyl ether is a solvent for cellulose nitrate and is widely used in lacquer formulation.[153] This ether, which is marketed under the trade name of "Cellosolve", is not a good solvent for the resins commonly incorporated in cellulose lacquers, however. The addition of other solvents is thus often necessary to ensure a clear solution of gums and cellulose ester. It has also been suggested as a solvent in the preparation of urea-formaldehyde resins,[154] for dispersing direct dyes,[155] for certain pharmaceutical preparations,[156] and as a constituent of liquids for use in hydraulic brake systems.[157] Davidson[158] recommended a thinner for pyroxylin lacquers which contains not more than 30 per cent of ethyl acetate and ethyl alcohol, nor more than 20 per cent of the monoethyl ether of ethylene glycol and its acetate, together with a hydrocarbon solvent. Admixture of this ether with lubricants, such as castor oil, is said to yield a lubricating liquid of superior viscosity-temperature characteristics.[159] The ether has also been proposed as a solvent in the preparation of ink for printing on photographic plates.[160] An aluminum derivative of this ether, aluminum ethylene glycoloxide monoethyl ether, is a catalyst for the conversion of aldehydes to esters by the Cannizzaro reaction.[161]

Ethylene glycol monoethyl ether acetate ("Cellosolve Acetate") is a colorless liquid boiling at 153° C., which is a solvent for cellulose nitrate, ester gum, mastic, kauri, and shellac. It does not dissolve cellulose acetate.

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[149] Davidson, U. S. Patent 1,644,417, Oct. 4, 1927; *Chem. Abs.*, 1927, **21**, 4068; U. S. Patent 1,834,050, Dec. 1, 1931; both patents assigned to Carbide and Carbon Chemicals Corp. Finkelstein, German Patent 545,172, 1924; *Chem. Abs.*, 1932, **26**, 3125; also U. S. Patents 1,801,340 and 1,801,341, Apr. 21, 1931; *Chem. Abs.*, 1931, **25**, 3502; all patents assigned to I. G. Farbenindustrie A.-G.

[150] Jordan, U. S. Patent 1,780,927, Nov. 11, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 179.

[151] Davidson, U. S. Patent 1,644,419, Oct. 4, 1927; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1927, **21**, 4068..

[152] *J.A.C.S.*, 1930, **52**, 3720.

[153] Davidson, U. S. Patent 1,644,420, Oct. 4, 1927; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1927, **21**, 4068; Shipley and Given, U. S. Patent 1,618,481, Feb. 22, 1927; assigned to Atlas Powder Co.; *Chem. Abs.*, 1927, **21**, 1194.

[154] I. G. Farbenindustrie A.-G., French Patent 641,420, 1926; *Chem. Abs.*, 1929, **23**, 1227.

[155] H. T. Böhme A.-G., British Patent 301,824, 1928; *Brit. Chem. Abs.* **B**, 1930, 321.

[156] I. G. Farbenindustrie A.-G., German Patent 446,290, 1925; German Patent 447,161, 1925.

[157] Bagley, U. S. Patent 1,779,460, Oct. 28, 1930; assigned to R. M. Hollingshead Co.; *Brit. Chem. Abs.* **B**, 1931, 522. *Cf.* I. G. Farbenindustrie A.-G., British Patent 348,642, 1930; *Brit. Chem. Abs.* **B**, 1931, 795.

[158] U. S. Patent 1,731,333, Oct. 15, 1929; assigned to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1929, 1047.

[159] I. G. Farbenindustrie A.-G., British Patent 348,642, 1930; *Brit. Chem. Abs.* **B**, 1931, 795.

[160] Middleton, U. S. Patent 1,833,086, Nov. 24, 1931; assigned to duPont Film Manufacturing Corp.; *Chem. Abs.*, 1932, **26**, 931.

[161] Young, U. S. Patent 1,630,593, May 31, 1927; assigned to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1927, 618.

Ethylene glycol monoethyl ether stearate, melting at 55° to 60° C., has been proposed as a plasticizer.[162] 2-Alkoxyethyl esters of stearic, oleic, or other fatty acids have been suggested as softeners for cellulose derivatives.[163]

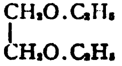
Ethylene glycol monopropyl ether has been suggested as a solvent in the preparation of lacquers, coating compositions and varnishes containing cellulose nitrate.[164] One of the advantages of the propyl ether is its lower miscibility with water than the corresponding methyl and ethyl ethers. Condensation products of naphthalene and the propyl ether have been proposed as wetting, cleansing, and emulsifying agents.[165]

Ethylene glycol mono-n-butyl ether is a high-boiling solvent of mild odor, known commercially as "Butylcellosolve". It is a solvent for cellulose nitrate and also for sandarac, mastic, kauri, cumarone resin, ester gum and elemi. It does not dissolve cellulose acetate or copal. It is especially recommended for brushing lacquers, for reducing the viscosity of lacquers and also for applying second coats over existing cellulose nitrate films.[166] It can be made by condensing ethylene oxide with n-butanol under pressure in the presence of sulphuric acid.[167] The solvent properties of various ethers have been discussed by Reid and Hofmann.[168]

Of the other mono-ethers of ethylene glycol, the monoamyl ethers have been proposed as solvents for cellulose nitrate in the manufacture of coating compositions.[169] The monophenyl ether [170] (boiling point, 237° C. at 760 mm., 165° C. at 80 mm.) and the monobenzyl ether [171] (boiling point, 132°-135° C. at 15 mm.) have also been prepared.[171a] The esters of various monoalkyl ethers of ethylene glycol with certain sulphonated carboxylic acids (e.g., sulphonated ricinoleic acid) have been suggested as wetting, foam-producing, and dispersing agents.[172] The tertiary phosphoric acid esters of monoalkyl or aryl ethers of ethylene, propylene, or butylene glycols can be prepared by the action of phosphorus oxychloride on the ether. They are said to be plasticizers in nitrocellulose lacquers and to be resistant to the action of light and low temperatures.[172a]

DIALKYL ETHERS OF ETHYLENE GLYCOL

Several dialkyl ethers of the lower glycols have been prepared. As solvents, however, they are not as satisfactory as the monoalkyl ethers. Ethylene glycol diethyl ether,



$$\begin{array}{l} CH_2O.C_2H_5 \\ | \\ CH_2O.C_2H_5 \end{array}$$

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[162] Kessler and Helfrich, U. S. Patent 1,739,315, Dec. 10, 1929; *Brit. Chem. Abs.* **B**, 1930, 939.

[163] Buckley, U. S. Patent 1,869,660, Aug. 2, 1932; assigned to E. I. duPont de Nemours and Co., Inc.; *Brit. Chem. Abs.* **B**, 1933, 822.

[164] Shipley and Given, U. S. Patent 1,618,482, Feb. 22, 1927; assigned to Atlas Powder Co.; *Chem. Abs.*, 1927, **21**, 1194

[165] I. G. Farbenindustrie A.-G., British Patent 302,258, 1927; *Brit. Chem. Abs.* **B**, 1929, 200.

[166] Durrans, "Solvents," Chapman and Hall, Ltd., London, 1930, 105.

[167] I. G. Farbenindustrie A.-G., British Patent 271,169, 1926; *Brit. Chem. Abs.* **B**, 1927, 571; Shipley and Given, U. S. Patent 1,618,483, Feb. 22, 1927; assigned to Atlas Powder Co.; *Chem. Abs.*, 1927, **21**, 1194.

[168] *Ind. Eng. Chem.*, 1928, **20**, 497.

[169] Shipley and Given, U. S. Patent 1,618,484, Feb. 22, 1927; assigned to Atlas Powder Co.; *Chem. Abs.*, 1927, **21**, 1194.

[170] I. G. Farbenindustrie A.-G., German Patent 459,311, 1926.

[171] Kayser and Schranz, U. S. Patent 1,651,458, Dec. 6, 1927; assigned to Winthrop Chemical Co.; *Chem. Abs.*, 1928, **22**, 845.

[171a] Conn, Collett and Lazzell (*J.A.C.S.*, 1932, **54**, 4370) prepared a number of aromatic esters of monoalkyl ethers of ethylene and diethylene glycols. It was found that when the reaction was carried out in furfural the yields were higher than in benzene.

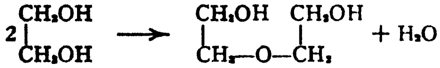
[172] H. T. Böhme A.-G., British Patent 351,456, 1930; *Brit. Chem. Abs.* **B**, 1931, 1003.

[172a] I. G. Farbenindustrie A.-G., German Patent 523,802, 1929; *Chem. Abs.*, 1931, **25**, 3667; British Patent 352,988, 1930; *Chem. Abs.*, 1932, **26**, 3391.

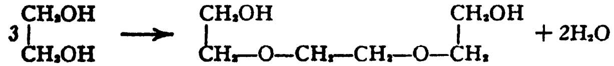
is a faintly odorous liquid (boiling point, 121° C.; D 0.853; and n^{20}_D 1.3914). It is considerably less soluble in water than the monoethyl ether and is a solvent for cellulose nitrate and for various gums, but not for cellulose acetate.[172b]

POLYGLYCOLS DERIVED FROM ETHYLENE GLYCOL

Polyglycols are substances derived from the simple 1,2-glycols by elimination of the elements of water from two or more molecules. They are produced by the action of dehydrating agents on glycols, during the hydration of olefin oxides to glycols (depending upon the proportions of olefin oxide and water employed), and by the interaction of olefin oxides with glycols. Diethylene glycol, triethylene glycol and polyethylene glycols as high as decaethylene glycol may be produced by elimination of water from ethylene glycol according to the reactions:

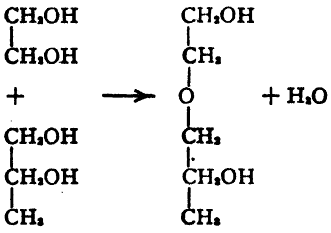


$$2\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} \longrightarrow \begin{array}{l}CH_2OH\quad CH_2OH\\ |\qquad\qquad\ |\\ CH_2{-}O{-}CH_2\end{array} + H_2O$$



$$3\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} \longrightarrow \begin{array}{l}CH_2OH\qquad\qquad\qquad\quad CH_2OH\\ |\qquad\qquad\qquad\qquad\qquad |\\ CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2\end{array} + 2H_2O$$

It is also possible to obtain mixed glycols. Thus, with ethylene and propylene glycols, ethylene propylene diglycol results according to the following condensation:



$$\begin{array}{c}CH_2OH\\ |\\ CH_2OH\\ +\\ CH_2OH\\ |\\ CH_2OH\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{c}CH_2OH\\ |\\ CH_2\\ |\\ O\\ |\\ CH_2\\ |\\ CH_2OH\\ |\\ CH_3\end{array} + H_2O$$

Since the polyglycols are both ethers and alcohols, they are solvents for cellulose esters, gums, and resins. The best solvent is apparently obtained when the number of ether groups is equal to the number of hydroxyl groups, as in triethylene glycol. The polyglycols are very hygroscopic, ranking with glycerol in this respect. This property does not seem to affect their solvent powers greatly and is advantageous in some applications, particularly in the production of plastics such as motion picture film and celluloid where their incorporation gives increased pliability and flexibility even in dry atmospheres. A whole series of mono- and di-alkyl ethers, and mono- and di-esters, exists for each polyglycol.

DIETHYLENE GLYCOL

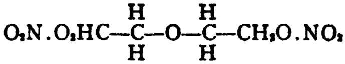
Diethylene glycol, $CH_2OH.CH_2.O.CH_2.CH_2OH$, is a colorless almost odorless liquid boiling at 244.5° C. at 760 mm. (D^{15}_{15} 1.1212; n^{20}_D 1.4475) and freezing at —10.5° C. Its heat of combustion is 566 kg.-cal. per mole. The viscosity of this compound is 0.50 and 0.27 poises at 15° C. and 27° C. respectively. At ordinary temperatures, it is freely miscible with water, lower alcohols, ethylene glycol, glacial acetic acid, acetone, furfural, pyridine, glycol diacetate, chloroform, nitrobenzene, and aniline but is immiscible with ether, benzene, toluene, carbon disulphide, and carbon tetrachloride. It is a solvent for cellulose nitrate and various dyes, but not for ester gum, shellac, cumarone resin, copals, or cellulose acetate. It absorbs more than its own weight of water in 9 days when kept in a closed space over water but undergoes no hydrolysis. Its density, viscosity, and refractive index at various temperatures have been determined by Rinkenbach.[173]

[172b] Davidson, *Ind. Eng. Chem.*, 1926, 18, 669.

Diethylene glycol can be obtained by the partial dehydration of ethylene glycol and by the action of ethylene oxide on glycol, but, according to Schrader,[174] the diethylene glycol which is marketed is a by-product of the hydration of ethylene oxide to glycol. Depending upon the relative amounts of oxide and water, triethylene, tetraethylene, and higher glycols may also be produced in smaller amounts.

Diethylene glycol has proved to be an ideal lubricant for wool spinning.[175] Impregnation of the fiber with this material renders unnecessary the use of oils and so obviates the costly process of scouring for oil elimination after spinning. Diethylene glycol has been suggested for use also in liquid heat-transfer media,[176] adhesives[177] and abrasive materials.[178]

Of the derivatives of this diglycol, the dinitrate,



$$O_2N.O_2HC-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-CH_2O.NO_2$$

is one of the more important. This was first prepared by Rinkenbach,[179] by nitration at below 10° C. in the presence of a nitrating mixture containing 25 per cent nitric acid, 5 to 10 per cent water, and the remainder, sulphuric acid. Yields of 60 to 70 per cent were obtained. The nitrating conditions were later improved to give a yield of about 85 per cent of the theoretical.[180] The pure dinitrate is a clear colorless liquid of greater fluidity than nitroglycerol. It is completely miscible with most organic solvents except ethyl alcohol, carbon tetrachloride and carbon disulphide. Its solubility in water is 4.1 grams per liter at 24° C. and it is only slightly hygroscopic. It freezes at —11.3° C. and has a specific gravity at 15° C. of 1.3908, refractive index of 1.4536, heat of combustion, 2798 gm.-cal. per gram at constant volume of 2792 gm.-cal. per gram at constant pressure, and a vapor pressure of 0.007 mm. at 22.4° C. It can be ignited only by heating and is less sensitive to shock than nitroglycerol or glycol dinitrate. When mixed with these compounds, it can be completely detonated and shows an explosive effect only a little less than either of them. It is, however, definitely toxic, the symptoms being similar to those produced by nitroglycerol.

Diethylene glycol monoacetate is a solvent for cellulose acetate and nitrate, rosin and gum camphor. It is miscible with water and aromatic hydrocarbons. The polyalkylene glycol esters may be made either by esterifying the polyglycol or by heating an olefin oxide with an organic acid in the presence of sulphuric acid (in the latter process, acetates of monoglycols are also formed).[181] Mixtures of the mono- and di-oleic and stearic acid esters of diethylene glycol (the oleate having p_H 5.0 and the stearate p_H 6.3) have been prepared. The former is a liquid insoluble in water but soluble in ethyl alcohol, esters and hydrocarbons. It can be used in weaving silk and rayon, and, in naphtha solution, for dry cleaning. Diglycol stearate is a solid, melting at 58°-60° C. Its dispersions in warm water serve to suspend abrasives, graphite, and pigments. Diglycol stearate is recommended also for the oiling and washing of wool and in the weaving of silk and rayon.[182]

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[173] *Ind. Eng. Chem.*, 1927, 19, 474.

[174] *Z. angew. Chem.*, 1929, 42, 541; *Chem. Abs.*, 1929, 23, 4444.

[175] *Chem. Met. Eng.*, 1930, 37, 61.

[176] Sherman, U. S. Patent 1,805,500, May 19, 1931; assigned to General Frigheatone Co.; *Chem. Abs.*, 1931, 25, 3746.

[177] Alexander, U. S. Patent 1,786,417, Dec. 30, 1930; *Chem. Abs.*, 1931, 25, 786.

[178] Leather, U. S. Patent 1,822,596, Sept. 8, 1931; assigned to Lea Manufacturing Co.; *Chem. Abs.*, 1931, 25, 5965.

[179] *Ind. Eng. Chem.*, 1927, 19, 925.

[180] Rinkenbach and Aaronson, *Ind. Eng. Chem.*, 1931, 23, 160; the nitration has been described also by Hough, Canadian Patent 325,098, 1932; *Chem. Abs.*, 1932, 26, 5578.

Mixed di-esters of diethylene glycol containing aliphatic acid radicals of less than 6 carbon atoms and (esterified with the second hydroxyl group) of more than 10 carbon atoms, are said to be fixatives for perfumes.[183] A product of this type, for example, is diethylene glycol monoacetate esterified with coconut oil acids, or oleic acid.

Diethylene glycol monoethyl ether is a liquid boiling at 198° C. at 760 mm. (D^{15}_{15} 0.9996, and n^{20}_D 1.4240). It has been marketed commercially under the trade name of "Carbitol". It may be manufactured by the condensation of ethylene oxide with ethylene glycol monoethyl ether at 70° to 250° C. under pressure.[184] It is a solvent for cellulose nitrate, and various gums and dyes and has found application in the manufacture of textile soaps, in dye-printing, and as a plasticizer. The monoalkyl ethers of the polyglycols have been proposed as constituents of anti-freeze solutions.[185]

Mono- and di-ethers of diethylene glycol have been proposed as wetting agents [186] and lubricants [187] in the treatment of cellulose textiles. The acetal of diethylene glycol monoethyl ether is suggested as a component of a cellulose acetate composition.[188] Leaper [188a] suggested using a solution of potassium hydroxide in "Carbitol" for the determination of saponification number of fats and waxes.

Diethylene glycol monobutyl ether (trade name, "Butylcarbitol") is a liquid of mild odor, boiling at 222° C., which dissolves cellulose nitrate and various gums but not cellulose acetate. It is miscible with water and hydrocarbons.

HIGHER POLYGLYCOLS

Triethylene glycol boils at 276° C. at 760 mm. Its monoethyl ether boils at 248° C. and has a specific gravity of 1.0566 at 15° C. The boiling points of tetraethylene glycol and its monoethyl ether are 230° C. at 25 mm., and 284° C. at 760 mm., respectively.[189] Both the polyglycols and their ethers are practically odorless.

The polyalkylene glycol ethers can be produced by the treatment of aliphatic alcohols with an excess of an olefin oxide in the presence of either acid or basic catalysts, such as strong acids, tertiary amines, and alkali alcoholates. A product, consisting mainly of ethyl ethers of tetraethylene glycol, is obtained by treating 230 parts of ethanol with 880 parts of ethylene oxide at 80° to 100° C. in the presence of 3 parts of sodium as catalyst.[190] Such products are said to be valuable assistants in the textile industry.[191]

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[181] Loehr, U. S. Patent 1,710,424, Apr. 23, 1929; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1929, 771.

[182] Bennett, *Ind. Chemist*, 1932, **8**, 223; *Brit. Chem. Abs.* **B**, 1932, 735; *Soap*, 1932, **8**, No. 1, 71; *Chem. Abs.*, 1932, **26**, 1577.

[183] Calvert, U. S. Patent 1,807,304, May 26, 1931; assigned to Van Schaack Bros. Chemical Works; *Chem. Abs.*, 1931, **25**, 4090.

[184] Davidson, U. S. Patent 1,633,927, June 28, 1927; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1927, **21**, 2704.

[185] I. G. Farbenindustrie A.-G., Swiss Patent 127,369, 1927.

[186] Chem. Fabrik vorm. Sandoz, British Patent 359,399, 1930; *Brit. Chem. Abs.* **B**, 1932, 99; Lier and Rheiner, U. S. Patent 1,851,394, Mar. 29, 1932; *Chem. Abs.*, 1932, **26**, 3121.

[187] Welch and Roberts, British Patent 365,566, 1930; assigned to British Celanese, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 418.

[188] Lawson, Canadian Patent 312,570, 1931; assigned to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 4403.

[188a] *Textile Colorist*, 1933, **55**, 601, 636; *Chem. Abs.*, 1933, **27**, 5206.

[189] Davidson, *Ind. Eng. Chem.*, 1926, **18**, 669.

Tetraethylene glycol (boiling point, 190° C. at 3 mm.) may be synthesized by the condensation of triethylene glycol with ethylene oxide under pressure.[192]

HIGHER 1,2-GLYCOLS

Propylene glycol (propane-1,2-diol, $CH_3.CHOH.CH_2OH$) is obtained from either of the propylene chlorohydrins by treatment with sodium bicarbonate solution under pressure. The production of this and other 1,2-glycols can be conducted by the general methods previously discussed in the section on ethylene glycol. The other method of preparing glycols, the hydrolysis of olefin dichlorides (or dihalides, generally), does not appear to be as applicable to the preparation of propylene glycol as to that of ethylene glycol, however. Wurtz[193] prepared propylene glycol by the action of silver acetate on propylene dibromide followed by hydrolysis of the diacetate formed, but hydrolysis of propylene dihalides either with lead oxide and water[194] or with aqueous potassium carbonate[195] leads to the formation of acetone and propionaldehyde as well as glycol. It is interesting to note that this glycol can be prepared by the hydration of allyl alcohol in the presence of 10 per cent aqueous hydrochloric acid,[196] thus:

$$CH_2OH.CH{=}CH_2 + H_2O \longrightarrow CH_2OH.CHOH.CH_3$$

Propylene glycol does not appear to offer any advantages over ethylene glycol in the various important applications of this latter substance. It has been proposed as a lubricant, either alone or mixed with other glycols, glycerol, or graphite, in refrigerating machines operating with ethane, propane, butane, or methyl and ethyl chlorides.[197]

Propylene glycol is a colorless sweet-tasting liquid boiling at 188° to 189° C. at 760 mm. and 96° to 98° C. at 21 mm. It is miscible with water and alcohol and dissolves in 12 to 13 volumes of diethyl ether. In chemical properties it closely resembles ethylene glycol. Thus, it readily forms both mono- and diesters and also mono- and di-alkyl ethers. Propylene glycol dinitrate is a colorless liquid closely resembling ethylene glycol dinitrate.[198] Heating with dilute acids to high temperatures converts the glycol into propionaldehyde and other substances. By heating propylene glycol to 170° C. with dilute sulphuric acid, Rix[199] obtained propionaldehyde, acetone, and methylacraldehyde. Linnemann[200] also obtained propionaldehyde by heating the glycol with very dilute hydrochloric acid to 220° C. As in the conversion of ethylene glycol into acetaldehyde under similar conditions, the reaction possibly takes place through the intermediate formation of an olefin oxide (or a dioxan derivative) which can isomerize to an aldehyde. Propylene glycol is converted into water and propionaldehyde by passing over pumice at 500° C., or over alumina at 250° to 260° C.[201]

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[190] Loehr, German Patent 542,765, 1925; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 3264.

[191] I. G. Farbenindustrie A.-G., British Patent 380,431, 1931; *Brit. Chem. Abs.* **B**, 1932, 1114.

[192] Sager, *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 388.

[193] *Loc. cit.*

[194] Eltekow, *J. Russ. Phys.-Chem. Soc.*, 1878, 10, 210; *Ber.*, 1878, 11, 989; *Chem. Soc. Abs.*, 1879, 36, 34.

[195] Hartmann, *J. prakt. Chem.*, 1877, (2) 16, 383; *Chem. Soc. Abs.*, 1878, 34, 211; *cf.* Völker and Belohoubeck, *Ber.*, 1876, 9, 924.

[196] Solonina, *J. Russ. Phys.-Chem. Soc.*, 1887, 19, 302; *Chem. Soc. Abs.*, 1888, 54, 806.

[197] Edwards, U. S. Patent 1,498,021, June 17, 1924; *Chem. Abs.*, 1924, 18, 2601.

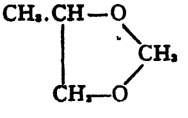
[198] Henry, *Ber.*, 1871, 4, 602.

[199] *Monatsh.*, 1904, 25, 267; *Chem. Soc. Abs.*, 1904, 86 (1), 465.

[200] *Ann.*, 1878, 192, 61; *Chem. Soc. Abs.*, 1878, 34, 776; *cf.* Linnemann, *Ann.*, 1872, 161, 58; Flavitsky, *J. Russ. Phys.-Chem. Soc.*, 1878, 10, 348; *Ber.*, 1878, 11, 1940; *Chem. Soc. Abs.*, 1879, 36, 136; *Bull. soc. chim.*, 1878, (2) 30, 22; *Chem. Soc. Abs.*, 1878, 34, 965.

Oxidation of propylene glycol with nitric or chromic acid results in the formation of glycollic, oxalic and acetic acids. Catalytic oxidation in the presence of a glowing platinum spiral was found to yield methylglyoxal and formaldehyde.[202]

Propylene glycol readily yields cyclic acetals by condensation with aldehydes. With formaldehyde, for example, in the presence of a little ferric chloride as catalyst, this glycol yields the ether,



boiling at 90° C.[203]

Propylene glycol, on treatment with sulphur monochloride or with gaseous hydrogen chloride, yields propylene chlorohydrin.[204] On dehydration it yields propylene oxide and a series of polyglycols in a manner similar to that of ethylene glycol. Various metallic derivatives (e.g., sodium compounds) of propylene glycol are also known.

Propylene glycol has a more acrid taste than glycerol or ethylene glycol. It exerts a local burning sensation on the tongue without, however, injuring the oral mucosa. It seems generally agreed that propylene glycol is much less toxic than ethylene glycol.[205] Intravenous fatal doses per kilogram of body weight were 16.8 milligrams for rats and 5.25 milligrams for rabbits.[206]

A considerable number of mono- and di-alkyl ethers of propylene glycol have been prepared. The monoalkyl ethers may be obtained by heating aliphatic alcohols under pressure with propylene oxide, whereas the corresponding di-ethers may be prepared from propylene glycol or chlorohydrin by condensation with a dialkyl sulphate in the presence of alkali.[207] The pure ethers, and their mixtures, may be used as solvents for gums, resins, and cellulose esters.[208] Table 106 gives the physical constants of some of the mono-ethers of propylene glycol.[209]

The monoaryl ethers, such as the monophenyl and monobenzyl ethers, are also solvents for cellulose esters. Tertiary esters of phosphoric acid with monoalkyl ethers of ethylene, propylene or butylene glycol have been suggested as softening and gelatinizing agents for cellulose acetate by Schönburg and Wick.[209a] The mono-ethers surpass the di-ethers in solvent power and may be used in conjunction with a wide variety of other solvents or diluents in the preparation of lacquers or the like.

[201] Nef, *Ann.*, 1904, **335**, 201; *Chem. Soc. Abs.*, 1905, **88** (1), 3; Ipatiev and Leontovitsch, *Ber.*, 1903, **36**, 2017.

[202] Trillat, *Bull. soc. chim.*, 1903, (3) **29**, 35; *Chem. Soc. Abs.*, 1903, **84** (1), 222; *Chem. Zentr.*, 1903, **1**, 438.

[203] Trillat and Cambier, *Compt. rend.*, 1894, **118**, 1277; *Chem. Soc. Abs.*, 1894, **66** (1), 487; *cf.* Henry, *Compt. rend.*, 1895, **120**, 107; *Chem. Soc. Abs.*, 1895, **68** (1), 266.

[204] Morley and Green, *J.C.S.*, 1885, **47**, 132.

[205] Hunt, *Ind. Eng. Chem.*, 1932, **24**, 361; *cf. ibid.*, 1932, **24**, 836.

[206] Seidenfeld and Hanzlik, *J. Pharm. Exp. Ther.*, 1932, **44**, 109; *Brit. Chem. Abs.* **A**, 1932, 425; *Chem. Abs.*, 1932, **26**, 2521.

[207] Davidson, U. S. Patent 1,730,061, Oct. 1, 1929; *Chem. Abs.*, 1929, **23**, 5474; British Patent 255,406, 1925; *Brit. Chem. Abs.* **B**, 1927, 428; both patents assigned to Carbide and Carbon Chemicals Corp.

[208] For example, dialkyl ethers of propylene glycol have been proposed by Jordan (U. S. Patent 1,865,191, June 28, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 4487) as ingredients of a nitrocellulose lacquer for application by spraying.

[209] Davidson, *Ind. Eng. Chem.*, 1926, **18**, 669.

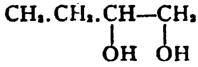
[209a] German Patent 549,220, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3919.

TABLE 106.—*Mono-Ethers of Propylene Glycol.*

Mono-Ether	Boiling Point ° C. at 736 mm.	D_{25}^{25}	n_D^{25}
Methyl	122.8	0.9335	1.4035
Ethyl	133.0	0.9090	1.4061
Isopropyl	141.5	0.8900	1.4062
n-Propyl	150.0	0.8970	1.4102
Isobutyl	161.3	0.8810	1.4112
n-Butyl	170.6	0.8890	1.4151
Isoamyl	183.3	0.8835	1.4182

Butylene Glycols. Three butylene-1,2-glycols are known:

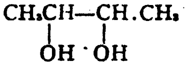
Butane-1,2-diol,



$$CH_3.CH_2.\underset{OH}{CH}—\underset{OH}{CH_2}$$

is the glycol corresponding with 1-butene and was obtained by Grabovsky and Saytzeff[210] from 1-butene dibromide. It boils at 191°-192° C. at 747 mm.

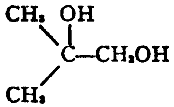
Butane-2,3-diol,



$$CH_3CH—CH.CH_3 \quad \text{with } OH \cdot OH$$

the glycol derived from 2-butene, boils at 183°-184° C. It can be obtained by the hydration of β-butylene oxide (3 volumes of water to 1 volume of oxide) at 100° C.[211]

2-Methylpropane-1,2-diol (also called isobutylene glycol),



is the glycol derived from isobutylene, from which hydrocarbon it can be prepared (though in poor yield) by oxidation with neutral aqueous permanganate.[212] It was made by Nevole[213] by heating isobutylene dibromide with aqueous potassium carbonate. Its boiling point is 176°-178° C. at 760 mm.

The higher glycols are of comparatively little interest and will not be considered in detail. In general chemical properties they resemble ethylene and propylene glycols. On dehydration they yield olefin oxides and heating with dilute acids at high temperatures tends to dehydrate them with the production of ketones, the dehydration often being accompanied by a molecular rearrangement. On being passed over a catalyst, for example, copper with an alkaline earth promoter at 210° to 220° C., isobutylene glycol forms methyl ethyl ketone and trimethylethylene glycol yields methyl isopropyl ketone.[214] 4-Hydroxy-2-butanone (acetylethyl alcohol) can be obtained by treating 1,3-butylene glycol with a dehydrogenating agent under reduced pressure at high temperature, according to Hilger.[215]

With some of the higher 1,2-glycols this conversion into ketones is also accompanied by an intramolecular change. For example, pinacone (tetramethylethylene glycol) is converted into the ketone, pinacolin, even under the influence of a weak acid (oxalic acid). The reaction can be represented as follows:

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[210] *Ann.*, 1875, **179**, 325; *Chem. Soc. Abs.*, 1876, **29**, 542.

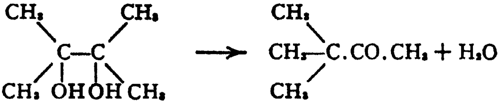
[211] Eltekow, *J. Russ. Phys.-Chem. Soc.*, 1882, **14**, 355; *Chem. Soc. Abs.*, 1883, **44**, 566.

[212] Wagner, *Ber.*, 1888, **21**, 1232.

[213] *Compt. rend.*, 1876, **83**, 228; *Bull. soc. chim.*, 1877, **27**, 463; *Chem. Soc. Abs.*, 1877, **31**, 58.

[214] I. G. Farbenindustrie A.-G., British Patent 318,124, 1928; *Brit. Chem. Abs.* **B**, 1929, 972.

[215] German Patent 568,546, 1931; *Chem. Abs.*, 1933, **27**, 2696; French Patent 740,647, 1932; *Chem. Abs.*, 1933, **27**, 2697; both assigned to I. G. Farbenindustrie A.-G.



Glycols similar to pinacone, i.e., glycols derived from tetralkylethylenes, also undergo this transformation.[216]

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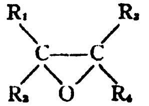
[216] Butlerow, *Ann.*, 1873, 170, 162; Nef, *Ann.*, 1901, 318, 37; Zelinsky and Zelikow, *Ber.*, 1901, 34, 3251; Tiffeneau, *Ann. chim.*, 1907, (8) 10, 373; Vörlander, *Ber.*, 1897, 30, 2266.

Chapter 23

Production, Properties, and Uses of Olefin Oxides and Their Derivatives

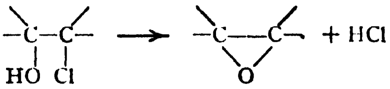
The olefin oxides are neutral substances of the general structure



where R_1, R_2, R_3, and R_4 may be hydrogen atoms or alkyl and aryl groups. These substances, particularly the ethylene and propylene homologues which are already finding applications in the industry, are capable of an astounding number of condensation reactions with other organic compounds and on this account will undoubtedly be used extensively in industrial organic synthesis.

PRODUCTION OF OLEFIN OXIDES

Olefin oxides may be produced by a number of reactions but the only important industrial method involves the elimination of hydrogen chloride from α-chlorohydrins by the use of alkalies. This reaction can be represented by



Wurtz[1] was the first to show that olefin oxides were obtained by the action of potassium hydroxide on chlorohydrins and obtained ethylene oxide in this way from ethylene chlorohydrin. This reaction is considered in greater detail later. Distillation of chlorohydrins over lead or zinc oxide yields only the corresponding aldehyde.[2]

Ethylene oxide may be prepared from ethylene chlorohydrin and mono-sodium glycol at 130° C.;[3] from ethylene iodide or ethylene bromide and silver oxide at 150° C. and 250° C., respectively;[4] and from ethylene bromide or ethylene chlorobromide and sodium oxide at 180° C.

Although theoretically olefin oxides should result from the dehydration of α-glycols, in actual practice this process usually produces a mixture of other substances such as aldehydes, ketones and dioxan derivatives. Thus, ethylene glycol on being heated either alone or with dehydrating agents such as zinc chloride or dilute acids yields acetaldehyde, dioxan and other substances according to the conditions. An example of the direct dehydration of an α-glycol to an olefin oxide has been reported by Gardeur,[5] who showed that triphenylethylene glycol in benzene solution could be dehydrated with phosphorus pentoxide to yield triphenylethylene oxide:

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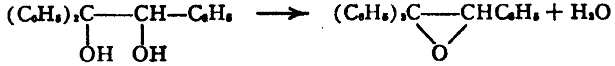
[1] *Ann.*, 1859, 110, 125; *Ann. chim.*, 1863, (3) 69, 317.

[2] Kaschirsky, *Ber.*, 1877, 10, 1104.

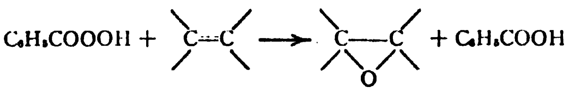
[3] Scheitz, *Z. für Chem.*, 1868, 379.

[4] Greene, *Compt. rend.*, 1878, 86, 624, 1141; *Chem. Soc. Abs.*, 1878, 34, 656; *Jahresber.*, 1877, 522.



$$(C_6H_5)_2C(OH)—CH(OH)—C_6H_5 \longrightarrow (C_6H_5)_2C\overset{O}{—}CHC_6H_5 + H_2O$$

In some cases the olefin oxides may be prepared by the direct oxidation of ethylene hydrocarbons. Thus, by passing isobutylene into an aqueous solution of iodine and potassium iodide at ordinary temperature, Pogorzelski[6] obtained a mixture of isobutylene oxide and trimethylcarbinol. Perbenzoic acid reacts with olefins in indifferent solvents to yield olefin oxides:[7]



By this interesting reaction, Prileschajew was able to prepare tetramethylethylene oxide, octylene oxide, diisobutylene oxide, decylene oxide, and pinene oxide from the corresponding unsaturated hydrocarbons.

Lenher[8] showed that ethylene and propylene oxides (as well as other substances) are formed in the reaction between an excess of ethylene or propylene, respectively, and oxygen, at 500° to 600° C. The best yield of ethylene oxide, namely 21 per cent of the total ethylene consumed, was obtained by passing a mixture of 80 volumes of ethylene and 10 volumes of oxygen through a pyrex tube at a temperature of about 535° C. with a contact time of 3 seconds.

Olefin oxides may be obtained indirectly by a number of other methods, such as the condensation of aldehydes with monochloroacetic esters and the action of nitrous acid on certain aminoalcohols, but these processes are of academic interest only.

As previously stated, the only industrially valuable method of manufacture of the lower olefin oxides is by elimination of hydrogen chloride from α-chlorohydrins in the presence of alkalies, the reaction discovered by Wurtz.[9] The procedure was commercialized by the Badische Co.[10] In their process, glycol formation was minimized by adding a warm solution of alkali to a warm solution of ethylene chlorohydrin.

The preparation of olefin oxides having from 5 to 8 carbon atoms per molecule was described by Walker.[11] The raw material is a cracked petroleum fraction, boiling from 35° to 125° C. From this fraction a mixture of chlorohydrin and hydrocarbons is obtained by treatment with hypochlorous acid. The hydrocarbons are separated by distillation and the chlorohydrins converted to the corresponding oxides by heating with slaked lime. Distillation of the alkali mixture yields an oily product, which after washing with 50 per cent caustic soda solution, dehydrating with potassium carbonate or calcium chloride, and redistilling gives a water-white mixture of olefin oxides. These oxides are insoluble in water, possess an ethereal odor, and are miscible with the usual organic solvents (alcohol, carbon tetrachloride and benzine). They are solvents for pyroxylin, varnish gums, asphalts and oils.

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[5] *Bull. acad. roy. Belg.*, (3) 34, 67; *Chem. Zentr.*, 1897, 2, 660.

[6] *J. Russ. Phys.-Chem. Soc.*, 1905, 37, 814; *Chem. Zentr.*, 1906, 1, 331.

[7] Prileschajew, *Ber.*, 1909, 42, 4811; 1910, 43, 959. *J. Russ. Phys.-Chem. Soc.*, 1910, 42, 1387; *Chem. Zentr.*, 1911, 2, 268; *J. Russ. Phys.-Chem. Soc.*, 1912, 44, 613; *Chem. Zentr.*, 1912, 2, 2090. For the preparation of the oxides of conjugated diolefins (isoprene and butadiene) by this reaction, see Pummerer and Reindel, *Ber.*, 1933, 66B, 335.

[8] *J.A.C.S.*, 1931, 53, 3737; 1932, 54, 1830.

[9] *Ann. chim.*, 1859, (3) 55, 427; 1863, (3) 69, 317.

[10] German Patent 299,682, 1915; *J.S.C.I.*, 1920, 39, 582A.

[11] U. S. Patent 972,952, Oct. 18, 1910; assigned to Maas and Waldstein; *Chem. Abs.*, 1911, 5, 150. See also British Patent 22,309, 1910; *Chem. Abs.*, 1911, 5, 3158; German Patent 254,858, 1910; *Chem. Abs.*, 1913, 7, 1587.

According to Brooks,[12] the yields of olefin oxides depend upon the concentration of the alkali and upon the rapid removal of the volatile oxides from the reaction mixture. Thus, when a 20 per cent solution of ethylene chlorohydrin is added to a 20 per cent solution of sodium hydroxide, only about 12 per cent of ethylene oxide is obtained. On the other hand, by using equal parts by weight of ethylene chlorohydrin (80 per cent chlorohydrin and 20 per cent water) and solid sodium hydroxide, the yield of oxide is 83 per cent. Quicklime also gives excellent yields, 70 to 90 per cent of the theory, when the chlorohydrin is substantially anhydrous. If much water is present the yield of oxide is very poor because of the formation of glycols and condensation products of unknown structure.

In the process mentioned above, the substantially anhydrous chlorohydrin is allowed to flow slowly onto solid caustic soda or quicklime, placed in an apparatus provided with means of stirring the contents and with outlets. The heats of formation of ethylene, propylene and butylene oxides are sufficient to distil the oxides almost as fast as they are formed. Means should be provided for heating the apparatus for making the higher olefin oxides. It is important to remove the oxides as fast as they are formed, which requires reduced pressure when working with the higher oxides. Ethylene, propylene, and butylene chlorohydrins react vigorously with caustic soda or lime at ordinary temperatures but most of the chlorohydrins containing 8 to 12 carbon atoms per molecule require several hours' heating at 100° to 150° C. to eliminate all the combined chlorine.

Burdick[13] expressed the opinion that the use of concentrated solutions of chlorohydrins is not essential. He obtained good yields (90 per cent or more) from solutions containing 10 per cent of chlorohydrins when the olefin oxide formed was removed at such a rate that no substantial accumulation of it occurred in the reaction mixture. This may be accomplished by heating the solution under atmospheric or reduced pressure, or in other ways. Thus, a 10 per cent ethylene chlorohydrin solution is heated to boiling in a kettle fitted with a rectifying column and a reflux condenser, and a strong solution of sodium hydroxide is added continuously. The oxide, together with steam, passes into the rectifying column where most of the steam is condensed while the ethylene oxide passes into a separate condenser cooled with brine. According to Burdick,[14] propylene oxide can be produced from dilute (10 per cent) solutions of propylene chlorohydrin in a similar manner, the yield in this case also being 90 per cent of the theoretical.

A continuous process for making olefin oxides from chlorohydrins was described by Walker, Schrader and Wiedbruck.[15] It involves the interaction of hot aqueous solutions of chlorohydrins with an alkali (milk of lime) under reduced pressures so that the liquid products boil at 80° C.

The solutions of alkali and chlorohydrins are simultaneously introduced into a reaction vessel divided into several compartments by baffles to promote good mixing. The mixture is heated by steam admitted at the bottom of the vessel. Steam and oxides distil and pass through a water condenser, in which the steam is condensed and flows back to the reaction vessel. The vapors of oxides are conducted through two coolers connected in series, the first of which is maintained at the higher temperature, to permit a partial separation of the oxides. Any uncondensed vapors escaping from the coolers are led through a scrubbing tower where they are reabsorbed by the incoming solution of chlorohydrins. Permanent gases leave the system through an outlet at the top of the scrubbing tower. The hot exhausted liquid from the reaction vessel is withdrawn through a heat exchanger, which serves to pre-heat the incoming chlorohydrin solution.

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[12] U. S. Patent 1,446,872, Feb. 27, 1923; assigned to Chadeloid Chemical Co.; *J.S.C.I.*, 1923, 42, 377A.

[13] U. S. Patent 1,589,358, June 22, 1926; *Chem. Abs.*, 1926, 20, 3015; Canadian Patent 245,153, 1924; *Chem. Abs.*, 1925, 19, 657; British Patent 236,379, 1924; *Chem. Abs.*, 1926, 20, 917. All patents assigned to Carbide and Carbon Chemicals Corp.

[14] U. S. Patent 1,589,359, June 22, 1926; assigned to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* B, 1926, 692.

[15] U. S. Patent 1,792,668, Feb. 17, 1931; assigned to T. Goldschmidt A.-G. See also British Patent 293,763, 1928; *Chem. Abs.*, 1929, 23, 1648; French Patent 656,996, 1928; *Chem. Abs.*, 1929, 23, 4229; German Patent 541,769, 1927; *Chem. Abs.*, 1932, 26, 2466.

The hydrolysis of ethylene chlorohydrin by aqueous alkaline solutions was also recommended by Saunders and Wignall.[16] A mixture of chlorohydrin vapors and steam is treated countercurrently with a stream of alkali solution. Ethylene oxide is the main product when a concentrated solution of sodium hydroxide is used. Substitution of sodium carbonate for sodium hydroxide results in the formation of glycol.

Relatively low temperatures and reduced pressures were recommended by Thole, Birch and Scott.[17] For example, aqueous solutions of ethylene chlorohydrin and sodium hydroxide are mixed at 10° to 20° C. and then introduced into a packed column at 30° to 50° C. and a pressure of 95 to 105 mm. of mercury. Ethylene oxide is liberated at once and collected in the form of its solid hydrate.

As previously mentioned, conversion of ethylene chlorohydrin to ethylene oxide may take place in the vapor phase. Oehme[18] suggested leading chlorohydrin vapors over solid alkalies. Aliphatic or hydroaromatic oxides are produced by passing the vapors of the corresponding 1,2-chlorohydrins, alone or mixed with steam, over catalysts such as magnesium oxide or copper phosphate, at 250° to 330° C.[19]

Ethylene oxide is said to result on conducting ethylene, air, steam and hydrogen over a catalyst heated to 150° to 400° C.[19a] Catalysts suggested are silver, bismuth or antimony, or a mixture containing two or more of the following metals: antimony, lead, bismuth, silver, nickel, tin or arsenic. The amount of carbon dioxide formed may be reduced by adding carbon dioxide to the reacting gases and the yield of ethylene oxide increased by lowering the pressure below atmospheric.

A method for the separation of individual olefin oxides from mixtures by fractional distillation under superatmospheric pressure was described by Finkelstein.[20]

PROPERTIES OF ETHYLENE OXIDE

Ethylene oxide is a colorless, highly volatile liquid which boils at 10.7° C., melts at —111.3° C. and has d_4^7 0.997. It is completely miscible with water and, like its homologues, is a good solvent for cellulose esters.[20a] On account of its extreme volatility, however, ethylene oxide is of little value as an industrial solvent. It is chiefly of importance for the multiplicity of its reactions which render it an admirable raw material for numerous organic syntheses.[21] In the following account it is possible to outline very briefly only the more important of these, which are, however, typical of the α-oxides as a class.

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[16] British Patent 286,850, 1927; assigned to British Dyestuffs Corp., Ltd.; *Brit. Chem. Abs.* **B**, 1928, 360.

[17] British Patent 374,864, 1932; assigned to Anglo-Persian Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1932, 878. See also French Patent 730,864, 1932; *Chem. Abs.*, 1933, 27, 312.

[18] German Patent 403,643, 1921; assigned to Chemische Fabrik Kalk G.m.b.H.; *J.S.C.I.*, 1925, 425B.

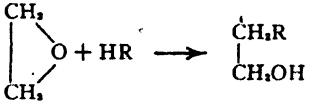
[19] Schering-Kahlbaum A.-G., British Patent 378,759, 1932; *Brit. Chem. Abs.* **B**, 1932, 1072; French Patent 728,849, 1931; *Chem. Abs.*, 1932, 26, 5963.

[19a] Soc. française de catalyse généralisée, French Patent 739,562, 1931; *Chem. Abs.*, 1933, 27, 2163; French Patent 41,811, 1933; *Chem. Abs.*, 1933, 27, 4546; addition to French Patent 739,562.

[20] Canadian Patent 285,920, 1928; *Chem. Abs.*, 1932, 23, 1138; British Patent 292,066, 1927; *Chem. Abs.*, 1929, 23, 1415; both patents assigned to I. G. Farbenindustrie A.-G.

[20a] Dreyfus, British Patents 391,769 and 391,828, 1931; *Brit. Chem. Abs.* **B**, 1933, 597.

Ethylene oxide, and α-oxides generally, reacts with numerous organic substances containing an easily replaceable hydrogen atom, such as alcohols, phenols, or amines, and also with water. The reaction can be summarized by the following:

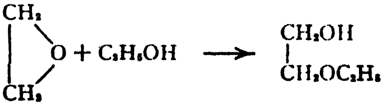


Reaction with Water

Ethylene oxide reacts slowly when heated with water in a sealed tube to yield ethylene glycol, a reaction first discovered by Wurtz.[22] The simultaneous formation of diethylene glycol and triethylene glycol as by-products was noted by Lourenço.[23] The reaction is greatly accelerated by catalysts such as sulphuric or hydrochloric acids,[24] particularly the former. According to Eltekov,[25] the ease of hydration of the lower olefin oxides depends mainly on the constitution of the oxide. For example, isopropylethylene oxide and sym-methylethylethylene oxide combine slowly with water, while isobutylene oxide reacts vigorously with it even at ordinary temperatures, with marked evolution of heat. In the industrial hydration of ethylene oxide to glycol [26] dilute sulphuric acid is used as a catalyst and it is necessary to take account of the considerable heat of reaction (about 25 kilogram-calories per mole). Youtz [27] stated that the formation of polyglycols during the hydration of olefin oxides can be avoided provided a large volume of water is present. He recommended 20 moles of water per mole of oxide.

Reaction with Alcohols and Phenols

The reaction between alcohols, or phenols, and olefin oxides is analogous to that with water and yields monoethers of the corresponding glycols. Thus, ethylene oxide when heated with ethyl alcohol yields ethylene glycol monoethyl ether: [28]



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[21] Bodforss, "Die Athylenoxyd," Encke, Stuttgart, 1920.

[22] *Ann.*, 1860, 113, 255. The kinetics of the reactions of ethylene oxides with water was studied dilatometrically by Brönsted, Kilpatrick and Kilpatrick, *J.A.C.S.*, 1929, 51, 428.

[23] *Ann. chim.*, 1863, (3) 67, 275.

[24] Bigot, *Ann. chim.*, 1891, (6) 22, 433; *Chem. Zentr.*, 1891, 1, 863. Henry, *Compt. rend.*, 1907, 144, 1404; *Chem. Soc. Abs.*, 1907, 93 (1), 745.

[25] *Ber.*, 1883, 16, Ref. 395.

[26] See Chapter 22 for methods of producing glycols.

[27] U. S. Patent 1,875,312, Aug. 30, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, 26, 5962.

[28] See for example, Young, U. S. Patent 1,696,874, Dec. 25, 1928; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1929, 23, 846; Loehr, German Patent 580,075, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 4814.

The similar reaction with phenol produces the monophenyl ether.[29] A small amount of sulphuric acid is effective in catalyzing this reaction,[30] probably by the intermediate formation of a sulphuric ester of ethylene glycol. Ethylene glycol monoethyl ether, propylene glycol monoethyl ether and ethylene glycol monophenyl ether are prepared[31] from the corresponding oxides by continuously passing the oxide mixed with the required alcohol or phenol under a pressure of 5 to 30 atmospheres through an enameled reaction tower heated to about 180° C. Catalysts for such reactions include dialkyl sulphates,[32] and certain acidulated hydrosilicates (especially those of aluminum) showing a p_H value less than 3 in aqueous suspensions.[33]

Various highly viscous ethers are obtained by condensing olefin oxides with polyhydric alcohols (e.g., glycerol, sorbitol, pentoses and ketoses) in the presence of sulphuric or boric acid catalysts.[34] Sorbitol heated with ethylene oxide in an autoclave at 140° C. for 12 hours yields sorbitol hexa-(β-hydroxyethyl) ether, and pentaerythritol similarly treated in the presence of boric acid, a syrupy ether. These ethers may be used as substitutes for polyhydroxy alcohols in paper making, dyeing, the explosives industry, textile processes, lubricants for machinery or as solvents or separating agents.[34a] Acylation with formic, acetic or benzoic acids or with polybasic acids, such as oxalic, succinic or phthalic, yields substances which may be employed as plasticizing materials. The esters formed with nitric acid may be used in the preparation of films, plastics, lacquers or explosives.

The extension of this reaction of olefin oxides with polyhydric alcohols to the production of hydroxyalkyl derivatives of the polymerized alcohols[35] (e.g., polyvinyl alcohol) and of the more complex carbohydrates (cellulose and starch) has attracted attention because the products are likely to prove useful in the textile industry. Catalysts for condensation of this kind, particularly those with cellulose and starch, include such basic materials as sodium hydroxide,[36] aqueous ammonia or hydroxyalkylamines,[37] and tertiary amines (dimethylaniline).[38] Mineral acids have been proposed also for catalyzing the combination of olefins with cellulose.[39] The hydroxyethers obtained by these methods can be converted into esters by heating with acid anhydrides in the presence of benzine.[40]

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[29] Roithner, *Monatsh.*, 1894, 15, 665; *Chem. Soc. Abs.*, 1895, **68** (1), 319.

[30] Fourneau and Ribas, *Bull. soc. chim.*, 1926, **39**, 1584; *Chem. Abs.*, 1927, **21**, 567; *Bull. soc. chim.*, 1927, **41**, 1046; *Chem. Abs.*, 1927, **21**, 3889.

[31] I. G. Farbenindustrie A.-G., British Patent 342,022, 1929; *Brit. Chem. Abs.* **B**, 1931, 433.

[32] Birch and Scott, U. S. Patent 1,882,564, Oct. 11, 1932; *Chem. Abs.*, 1933, **27**, 731; British Patent 367,353, 1930; *Brit. Chem. Abs.* **B**, 1932, 591; both patents assigned to Anglo-Persian Oil Co., Ltd. Also French Patent 725,245, 1931; *Chem. Abs.*, 1932, **26**, 4825. Davidson, U. S. Patent 1,614,883, Jan. 18, 1927; assigned to Carbide and Carbon Chemicals Co.; *Chem. Abs.*, 1927, **21**, 746.

[33] I. G. Farbenindustrie A.-G., British Patent 354,357, 1930; *Brit. Chem. Abs.* **B**, 1932, 12; French Patent 39,773, 1931, addition to 610,282; *Chem. Abs.*, 1932, **26**, 4826; German Patent 558,646, 1930; *Chem. Abs.*, 1933, **27**, 512.

[34] I. G. Farbenindustrie A.-G., British Patent 317,770, 1928; *Brit. Chem. Abs.* **B**, 1929, 886; French Patent 650,973, 1928; *Chem. Abs.*, 1929, **23**, 3232.

[34a] Schmidt and Meyer, U. S. Patent 1,922,459, Aug. 15, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 5082.

[35] I. G. Farbenindustrie A.-G., British Patent 364,323, 1929; *Chem. Abs.*, 1933, **27**, 1641; French Patent 713,427, 1931; *Chem. Abs.*, 1932, **26**, 1616.

[36] I. G. Farbenindustrie A.-G., German Patents 527,617, 1929; *Chem. Abs.*, 1931, **25**, 5287; 535,849, 1929; *Chem. Abs.*, 1932, **26**, 1119; 542,867, 1929, 548,456 and 550,428, 1930; *Chem. Abs.*, 1932, **26**. 4174. British Patents 358,510 and 359,618, 1930; *Brit. Chem. Abs.* **B**, 1932, 224. French Patent 39,765, 1931, addition to 700,880; *Chem. Abs.*, 1932, **26**, 4951. Schorger, U. S. Patent 1,863,208, June 14, 1932; assigned to C. F. Burgess Laboratories, Inc.; *Chem. Abs.*, 1932, **26**. 4174; also British Patent 389.534, 1931; *Brit. Chem. Abs.* **B**, 1933, 543. British Patent 392,206, 1933; *Chem. Abs.*, 1933, **27**, 4927. For the preparation of mixed cellulose ethers, see Hagerdorn, Ziese, Reyle and Bauer, U. S. Patent 1,876,920, Sept. 13, 1932; *Chem. Abs.*, 1933, **27**, 101; Hagerdorn and Rossbach, U. S. Patent 1,877,856, Sept. 20, 1932; *Chem. Abs.*, 1933, **27**, 413; both patents assigned to I. G. Farbenindustrie A.-G.

[37] I. G. Farbenindustrie A.-G., French Patent 708,538, 1930; *Chem. Abs.*, 1932, **26**, 3667; Suida, Austrian Patent 125,234, 1931; *Chem. Abs.*, 1932, **26**, 1439.

[38] I. G. Farbenindustrie A.-G., British Patent 358,510, 1930; *Brit. Chem. Abs.* **B**, 1932, 224. *Cf.* Dreyfus, British Patent 396,796, 1932; *Brit. Chem. Abs.* **B**, 1933, 860.

Shoruigin and Rimashevskaya[40a] studied the properties of cellulose hydroxyethyl ether and its acetate. Bleached cotton (linters), viscose silk and copper-ammonium silk were mercerized and then heated for 18 hours at 30° C. with ethylene oxide. The product was dissolved in water and precipitated from solution with acetone, giving a fine white flocky material which decomposed at about 245° to 250° C. This substance was soluble in water, acetic acid, and fused phenol, but insoluble in acetone, alcohol and ether. The iodine number varied from 2.40 to 3.88 and the compound appeared to correspond with the formula $C_6H_7O_2(OH)_2OCH_2CH_2OH$. An acetic acid-acetone mixture containing sulphuric acid, gave a triacetate which decomposed at 192° to 104° C. It was soluble in acetone, chloroform and acetic acid and its iodine number was 5.2-5.3.

The glycol monoalkyl esters, or their derivatives, have been suggested as sealing liquids for gasometers or as cooling liquids (to reduce the freezing point of water) for internal-combustion engines.[41]

By employing a considerable excess of olefin oxide over that required to form the monohydroxy ether of the reacting alcoholic compound, it is possible to make polyolefin glycol ethers as the main products. Loehr[42] suggested the use of sodium as a catalyst for such a reaction. Introduction of ethylene oxide into anhydrous ethyl alcohol, containing a small proportion of sodium, leads to the formation of the ethyl ether of tetraethylene glycol and its higher homologues. Monophenyl and monotolyl ethers of the polyolefin glycols can be prepared by passing an excess of the olefin oxide into the fused phenol to which sodium hydroxide has been added.[43]

The esterification or etherification products of non-carbohydrate organic compounds containing hydroxyl or carboxyl groups (such as alcohols from the catalytic reduction of oils and fats, or from oxidized paraffin wax, or castor oil, oleic or palmitic acids) with polyethylene glycols or their monoethers or monoesters (or an equivalent quantity of ethylene oxide or ethylene chlorohydrin) have been suggested as wetting, foaming, or dispersing agents.[43a]

The production of polyolefin glycol ethers by condensation of olefin oxides with glycols has been described by Davidson.[44] He suggested the use of these ethers,[45] as well as esters of the ethers of glycols and polyglycols,[46] in paint, varnish and lacquer removers.

REACTION WITH HYDROGEN HALIDES

Ethylene oxide reacts not only with anhydrous hydrogen chloride but also with aqueous solutions of certain metallic chlorides to form chlorohydrin. The reaction of the olefin oxides with hydrogen chloride is a general one, although it often yields a mixture of isomeric chlorohydrins. Hydrogen bromide reacts in a similar manner to yield bromohydrins, and in some cases hydrogen iodide combines with the oxides to give iodohydrins.[47]

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[39] I. G. Farbenindustrie A.-G., German Patent 542,867, 1929; *Chem. Abs.*, 1932, **26**, 4174. Suida (Austrian Patent 125.229. 1931; *Chem. Abs.*, 1932, **26**, 1436) treated comminuted wood with an alkylene oxide at 20°-180° C. in the presence of a tertiary base or a weak acid or acid salt to obtain products which could be molded.

[40] I. G. Farbenindustrie A.-G., British Patent 365,250, 1929; *Chem. Abs.*, 1933, **27**, 1753.

[40a] *Ber.*, 1933, **66**, 1014.

[41] Jordan, German Patent 468,917, 1926; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 4372.

[42] German Patent 542,765, 1925; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3264.

[43] Loehr, German Patent 519,730, 1925; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3359.

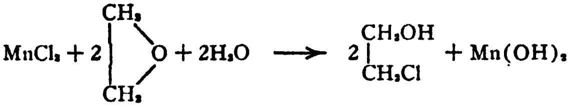
[43a] I. G. Farbenindustrie A.-G., British Patent 380,431, 1931; *Brit. Chem. Abs.* **B**, 1932, 1114.

[44] U. S. Patent 1,633,927, June 28, 1927; assigned to Carbide and Carbon Chemicals Co.; *Chem. Abs.*, 1927, **21**, 2704.

[45] U. S. Patent 1,812,321, June 30, 1931; assigned to Carbide and Carbon Chemicals Co.; *Chem. Abs.*, 1931, **25**, 4984.

[46] U. S. Patent 1,812,322, June 30, 1931; assigned to Carbide and Carbon Chemicals Co.; *Chem. Abs.*, 1931, **25**, 4984.

The reaction of ethylene oxide, and olefin oxides generally, with aqueous solutions of hydrolyzable metallic halides is made the basis of a test for such oxides.[48] With chlorides of aluminum, magnesium, iron, tin, zinc and manganese in neutral solutions, ethylene oxide absorbs the acid freed by dissociation and hydrolysis, and the metallic hydroxide is precipitated. This reaction can be illustrated as follows:



The appearance of a precipitate in a controlled test solution is evidence of the presence of an olefin oxide. Although magnesium chloride solution has been most frequently used,[49] Lenher[50] concluded that a saturated aqueous solution of manganous chloride gives the more sensitive and easily controlled test.

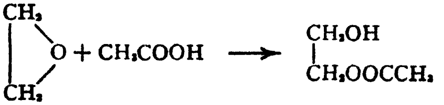
In ether solutions ethylene oxide reacts with magnesium bromide to give a product having the formula $CH_2BrCH_2OMgBr.(C_2H_5)_2O$. Hydrolysis of this substance yields bromohydrin and magnesium bromide and hydroxide.[51] This latter reaction may be represented by:

$$2CH_2BrCH_2OMgBr.(C_2H_5)_2O + 2H_2O \longrightarrow CH_2BrCH_2OH + MgBr_2 + Mg(OH)_2 + 2(C_2H_5)_2O$$

Ethylene oxide can combine with ethylene chlorohydrin in the presence of a small amount of sulphuric acid to yield dioxan as well as β-chloroethyl β-hydroxyethyl ether and ββ′-chloroethoxyethyl β-hydroxyethyl ether.[52]

Reaction with Organic Acids and Acid Anhydrides

The reaction of olefin oxides with organic acids appears to be a fairly general method for the preparation of the mono-esters of the corresponding glycol, but if an organic acid anhydride is employed the di-ester of the glycol is formed. By heating ethylene oxide with glacial acetic acid, Wurtz[53] obtained ethylene glycol monoacetate and the diacetate from acetic anhydride.[54] These reactions may be represented as follows:



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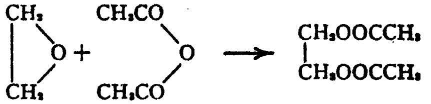
[47] Wurtz, *Ann. chim.*, 1863, (3) 69, 317, 355.
[48] Walker, *Ber.*, 1901, 34, 4115; Wurtz, *Ann.*, 1860, 116, 252.
[49] Mulliken. "Identification of Pure Organic Compounds." John Wiley and Sons, New York, 1905, 1, 160.
[50] *J.A.C.S.*, 1931, 53, 3739.
[51] Ribas and Tapia. *Anal. Fis. Quim.*, 1932, 30, 778; *Brit. Chem. Abs.* A, 1933, 48.
[52] Fourneau and Ribas, *Bull. soc. chim.*, 1927, (4) 41, 1046; *Brit. Chem. Abs.* A, 1927, 1052.
[53] *Ann.*, 1860, 116, 249.
[54] *Ann.*, 1860, 113, 255.



These important reactions, which constitute industrial methods for making the esters of the lower glycols, are catalyzed by small amounts of sulphuric acid[55] and also by ferric chloride.[56] A continuous process for the manufacture of ethylene glycol monoacetate consists in passing a mixture of ethylene oxide and glacial acetic acid, under pressures of 5 to 30 atmospheres, through a reaction tower heated to 130° C.[57]

Wax-like bodies are obtained on heating alkylene oxides with a mixture of oxidized montan wax and naphthenic acids.[58]

Catalysts for accelerating the combination of olefin oxides with carboxylic acids consist of acidulated hydrosilicates (particularly those of aluminum) which, on dispersion in water, exhibit a p_H value of not more than about 3.[59] Thus, on slowly introducing 80 parts of ethylene oxide into a mixture of 20 parts of the hydrosilicate "Tonsil AC" with 400 parts of glacial acetic acid at 25° C., a vigorous exothermic reaction takes place. The mixture is maintained at 50° to 55° C. (by cooling) and is stirred for 15 minutes after all the oxide has been added. On filtering and distilling, the products are 180 parts of a mixture of ethylene glycol mono- and di-acetates together with a small amount of high-boiling substances, presumably polyethylene glycol acetates.

Sodium benzoate has been suggested as a catalyst for the reaction between ethylene oxide and fused benzoic acid.[60]

Dibasic acids (phthalic, succinic or tartaric) are converted into their corresponding ethyl esters by heating with ethylene oxide at 60° to 70° C.[61] Rosin reacts with oxide at 160° to 170° C. under pressure to yield resins which may be employed in the manufacture of lacquers and varnishes.[62]

REACTION WITH AMMONIA AND AMINES

Ethylene oxide reacts energetically with dilute or concentrated ammonia solution to yield a mixture of three basic substances, mono-, di-, and tri-ethanolamines,[63] having the formulas $NH_2CH_2CH_2OH$, $NH(CH_2CH_2OH)_2$, and $N(CH_2CH_2OH)_3$, respectively. It was shown by Knorr[64] that the presence of a small proportion of water is essential to this reaction, since pure ethylene oxide does not react with dry ammonia. These reactions are of industrial importance since the ethanolamines are used on a substantial scale as emulsifying agents and in other ways. A discussion of the properties of the simple ethanolamines is given later.

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[55] Jorlander, *Ber.*, 1917, 50, 407. Japp and Michie, *J.C.S.*, 1903, 83, 279. Hoering, *Ber.*, 1905, 38, 3483; 1907, 40, 1099.

[56] Knoevenagel, *Ann.*, 1914, 402, 111.

[57] I. G. Farbenindustrie A.-G., British Patent 342,022, 1929; *Brit. Chem. Abs.* B, 1931, 433.

[58] Rodrian, Bauer and Doser, German Patent 565,966, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 2595.

[59] I. G. Farbenindustrie A.-G., British Patent 354,357, 1931; *Brit. Chem. Abs.* B, 1932, 12; French Patent 39,773, 1931; *Chem. Abs.*, 1932, 26, 4826.

[60] Steimmig and Ulrich, U. S. Patent 1,817,425, Aug. 4, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 5433.

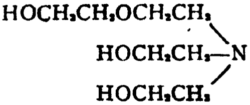
[61] Webel, U. S. Patent 1,883,182, Oct. 18, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 731.

[62] Schmidt and Meyer, German Patent 561,626, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 1219.

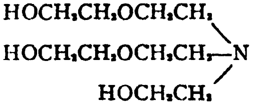
[63] Wurtz, *Ann.*, 1860, 114, 51.

[64] *Ber.*, 1899, 32, 729.

The reaction between α-oxides (particularly ethylene oxide) and ammonia in aqueous solution can be made to yield complex compounds by using a large excess of the oxide. Such substances are probably formed by further action of the excess olefin oxide on the simple ethanolamine initially formed. Thus, a mixture of mono-, di-, and tri-hydroxyethyl ethers of triethanolamine is obtained by the action of an excess (at least 4 moles per mole of base) of ethylene oxide on aqueous ammonia.[65] These compounds possess the following formulas:



monohydroxyethyl ether



dihydroxyethyl ether

$$(HOCH_2CH_2OCH_2CH_2)_3N$$

trihydroxyethyl ether

Since from a theoretical standpoint such condensation reactions can be extended almost indefinitely, the number of higher condensation products would seem to be almost limitless.

In general, the homologues of ethylene oxide react less readily with ammonia. Krassuski and Duda[66] found that hexene-2 oxide reacts very slowly with ammonia at ordinary temperatures. After several hours' heating in a sealed tube at 100° C. the product was mainly the monohexanolamine,

$$CH_3CH(OH)CH(NH_2)CH_2CH_2CH_3$$

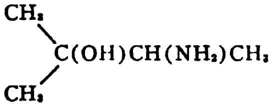
or

$$CH_3CH(NH_2)CH(OH)CH_2CH_2CH_3$$

with some secondary amine as a by-product. Under similar conditions tetramethylethylene oxide yielded the monoamine,

$$(CH_3)_2C(OH)C(NH_2)(CH_3)_2$$

Trimethylethylene oxide reacted very slowly with 33 per cent aqueous ammonia (not at all with anhydrous ammonia) at ordinary temperatures, but heating at 100° C. for some hours resulted in the formation principally of the monoamine



with only small amounts of the secondary product. In the same way, isobutylene oxide reacted with concentrated aqueous ammonia to give the aminotrimethylcarbinol,

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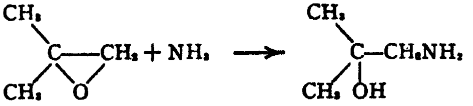
[65] I. G. Farbenindustrie A.-G., British Patent 364,000, 1930; *Brit. Chem. Abs.* **B**, 1932, 495; French Patent 713,382, 1931; *Chem. Abs.*, 1932, **26**, 1733; French Patent 713,998, 1931; *Chem. Abs.*, 1932, **26**, 1619.

[66] *J. pr. Chem.*, 1908, (2) **77**, 84; *Chem. Abs.*, 1908, **2**, 2226; *J. Russ. Phys.-Chem. Soc.*, 1907, **36**, 1061; *Chem. Abs.*, 1908, **2**, 1124.



together with large amounts of the secondary compound and a small quantity of the tertiary amine.

Cyclohexene oxide reacts similarly with ammonia to yield 2-aminocyclohexanol,[67] and cyclopentene oxide and aqueous ammonia at 110° C. form trans-2-aminocyclopentanol.[68]

Primary and secondary amines can be condensed with olefin oxides, just as ammonia can, to yield the corresponding alkyl- and aryl-amino alcohols. The presence of water exerts a remarkable influence and is frequently absolutely essential. In some instances, as in the reaction between monomethylaniline and ethylene oxide to produce the amino alcohol having the formula

$$C_6H_5N(CH_3)CH_2CH_2OH$$

water does not appear to exert any influence on the yield.[69] A series of alkylamino alcohols has been prepared by condensing ethylene oxide with aliphatic amines.[70] Of the simple condensation products of olefin oxides with cyclic bases, cyclohexylethanolamine is prepared from cyclohexylamine and ethylene oxide.[71] The hydroxyalkylamines made from primary or secondary amines (containing at least one chain of more than 8 carbon atoms) and olefin oxides are said to be wetting agents.[72] Condensation products of hydroxyl-free amines or amides (such as octadecylamine or amides of oleic, stearic, naphthenic acids or p-toluenesulphonic acid) and polyethylene glycols (or a corresponding quantity of ethylene oxide or halohydrin) have been suggested as textile reagents.[72a]

Ethylene oxide does not react with pure dry diethylamine, but in the presence of water, or better of methyl or ethyl alcohol, a smooth and rapid absorption of the oxide takes place.[73] The initial product is β-diethylaminoethanol (Formula I, below), which can be prepared in good yields by passing the gaseous oxide into a solution of diethylamine (in water or alcohol) at 45° to 60° C. until about 0.5 mole of oxide is absorbed per mole of amine. As the proportion of ethylene oxide is increased, the amount of unreacted amine diminishes, but the products contain a number of substances boiling above β-diethylaminoethanol. From these higher boiling compounds may be separated the mono-β-diethylaminoethyl ether of ethylene glycol (Formula II) and the mono-β-diethylaminoethyl ether of diethylene glycol (Formula III). The two highest boiling fractions appeared to consist of the mono-β-diethylaminoethyl ether of triethylene glycol (Formula IV) and tetraethylene glycol (Formula V), respectively. These substances represent the progressive addition of ethylene oxide molecules to diethylamine and their formation may be indicated as follows:

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[67] Brunel, *Compt. rend.*, 1903, **136**, 383; *Chem. Zentr.*, 1903, **1**, 711; *Compt. rend.*, 1903, **137**, 198; *Chem. Zentr.*, 1903, **2**, 665.

[68] Godchot and Mousseron, *Compt. rend.*, 1932, **194**, 2061; *Brit. Chem. Abs.* **A**, 1932, 844.

[69] Gabel, *Bull. soc. chim.*, 1927, **41**, 936; *Chem. Abs.*, 1928, **22**, 229.

[70] Knorr and Schmidt, *Ber.*, 1898, **31**, 1072. Knorr, *Ber.*, 1899, **32**, 729. Knorr and Matthes, *Ber.*, 1901, **34**, 3482. Matthes, *Ann.* 1901, **315**, 104; 1901, **316**, 311.

[71] Schmidt, Seydel and Meyer, U. S. Patent 1,845,563, Feb. 16, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2198.

[72] Hentrich and Keppler, German Patent 552,268, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 4426.

[72a] I. G. Farbenindustrie A.-G., British Patent 380,851, 1931; *Brit. Chem. Abs.* **B**, 1933, 54.

[73] Horne and Shriner, *J.A.C.S.*, 1932, **54**, 2925. Headlee, Collett and Lazzell (*J.A.C.S.*, 1933, **55**, 1066) have prepared similar compounds by successive additions of ethylene oxide to diethylamine. The physical properties of their products, however, differed from those reported by Horne and Shriner. Some indications were obtained that ethylene oxide reacts with the solvent, methyl alcohol.

$$(C_2H_5)_2NH$$

$$\downarrow \text{(+ ethylene oxide)}$$

$$(C_2H_5)_2NCH_2CH_2OH \qquad \text{(Formula I)}$$

$$\downarrow \text{(+ ethylene oxide)}$$

$$(C_2H_5)_2NCH_2CH_2OCH_2CH_2OH \qquad \text{(Formula II)}$$

$$\downarrow \text{(+ ethylene oxide)}$$

$$(C_2H_5)_2N(CH_2CH_2O)_2CH_2CH_2OH \qquad \text{(Formula III)}$$

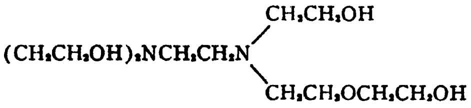
$$\downarrow \text{(+ ethylene oxide)}$$

$$(C_2H_5)_2N(CH_2CH_2O)_3CH_2CH_2OH \qquad \text{(Formula IV)}$$

$$\downarrow \text{(+ ethylene oxide)}$$

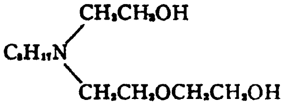
$$(C_2H_5)_2N(CH_2CH_2O)_4CH_2CH_2OH \qquad \text{(Formula V)}$$

Many other examples of this progressive addition of olefin oxide molecules to primary and secondary amines are known. Hydroxylated ethers of tertiary β-hydroxyalkylamines are made by condensing an amine (primary or secondary) with an excess (at least n + 1 moles of olefin oxide for n replaceable hydrogen atoms in the base) of olefin oxide in an aqueous medium.[74] Condensation of ethylene oxide and ethylenediamine in the molar proportions of 5 : 1 yields a material of the constitution,



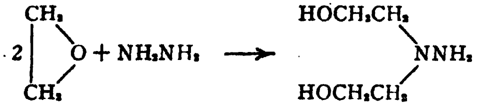
$$(CH_2CH_2OH)_2NCH_2CH_2N\begin{cases}CH_2CH_2OH\\CH_2CH_2OCH_2CH_2OH\end{cases}$$

The product of the reaction of 1 mole of octylamine with 3 moles of ethylene oxide has been assigned the formula[75]



$$C_8H_{17}N\begin{cases}CH_2CH_2OH\\CH_2CH_2OCH_2CH_2OH\end{cases}$$

Hydrazine and its derivatives can unite in a similar way with olefin oxides. Thus, hydrazine itself readily combines with the oxide to give bis-ethanol-hydrazine,[76]



Phenylhydrazine reacts with ethylene oxide to yield a more complex product.[77]

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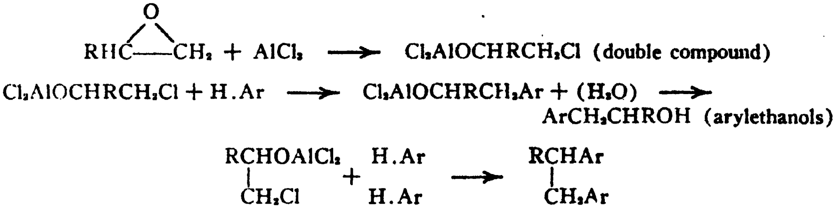
[74] I. G. Farbenindustrie A.-G., British Patent 364,000, 1930; *Brit. Chem. Abs.* B, 1932, 495.
[75] I. G. Farbenindustrie A.-G., British Patent 364,104, 1930; *Brit. Chem. Abs.* B, 1932, 495.
[76] Knorr and Brownsdon, *Ber.*, 1902, 35, 4474.
[77] Roithner, *Monatsh.*, 1894, 15, 665; *Chem. Soc. Abs.*, 1895, 68 (1), 319.

DIRECT ADDITION OF OLEFIN OXIDES TO HYDROCARBONS

The condensation of ethylene oxide with aromatic hydrocarbons, under the influence of aluminum chloride or other Friedel-Crafts condensing agent, was demonstrated by the work of Schaarschmidt, Hermann and Szemzö.[78] They obtained dibenzyl, together with a small amount of β-phenylethanol, by passing a mixture of ethylene oxide and hydrogen chloride into a mixture of benzene and aluminum chloride. This reaction has been re-examined by Smith and Natelson,[79] who also obtained dibenzyl and its homologues, together with phenylethanols as by-products. The formation of intermediate double compounds between the olefin oxide and anhydrous aluminum chloride probably constitutes the first phase of the reaction. These double compounds then react with the aromatic hydrocarbon in one of two ways as follows:



$$RHC\overset{O}{\text{——}}CH_2 + AlCl_3 \longrightarrow Cl_2AlOCHRCH_2Cl \text{ (double compound)}$$

$$Cl_2AlOCHRCH_2Cl + H.Ar \longrightarrow Cl_2AlOCHRCH_2Ar + (H_2O) \longrightarrow ArCH_2CHROH \text{ (arylethanols)}$$

$$\begin{array}{l} RCHOAlCl_2 \\ | \\ CH_2Cl \end{array} + \begin{array}{l} H.Ar \\ \\ H.Ar \end{array} \longrightarrow \begin{array}{l} RCHAr \\ | \\ CH_2Ar \end{array}$$

(R represents a hydrocarbon radical or hydrogen and Ar an aromatic nucleus). By the addition of 1 mole of ethylene oxide to a well-cooled mixture of 1 mole of anhydrous aluminum chloride and 6 moles of benzene followed by decomposition of the reaction mixture with water, Smith and Natelson isolated 65 per cent of dibenzyl and 5 per cent of β-phenylethanol.

This condensation has been extended to the preparation of numerous hydroxy derivatives of aliphatic, alicyclic, aromatic or heterocyclic compounds (not containing reactive amino, hydroxy or carboxyl groups). Reaction is effected at temperatures varying from —10° to 100° C., best under pressure, and in the presence of a condensing agent such as aluminum halides, boron trifluoride or anhydrous ferric chloride.[80] Inert organic diluents (carbon disulphide or tetrachloride) are used. Examples are the condensation of ethylene oxide with benzene to yield β-phenylethanol, with n-pentane to form n-heptanol, with naphthalene to give β-naphthylethanol, and with cyclohexane to produce β-cyclohexylethanol. When the oxide is condensed with kerosene a mixture of primary alcohols is obtained. Under similar conditions ethylene chloride and oxide form a mixture of ethylene chlorohydrin and 1,4-butylene chlorohydrin. With pyridine this oxide yields hydroxyethylpyridines.

REACTION WITH CYANIDES

When olefin oxides are heated for some time with anhydrous hydrogen cyanide, or with solutions or suspensions of cyanides, combination takes place with the formation of cyanohydrins[81]:

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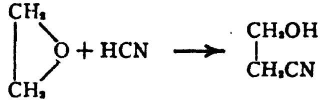
[78] *Ber.*, 1925, 58, 1914.

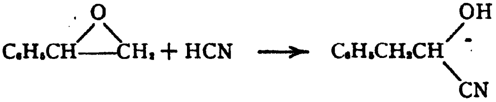
[79] *J.A.C.S.*, 1931, 53, 3476.

[80] I. G. Farbenindustrie A.-G., British Patent 354,992, 1930; *Brit. Chem. Abs.* B, 1932, 12; French Patent 716,604, 1931; *Chem. Abs.*, 1932, 26, 2198. See also Hitch and Dahlen, U. S. Patents 1,893,283 and 1,893,284, Jan. 3, 1933; both patents assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1933, 27, 2298.

[81] Erlenmeyer, *Ann.*, 1878, 191, 269; Hörmann, *Ber.*, 1879, 12, 23.



The reaction occasionally takes an abnormal course as styrene, for example, yields the cyanohydrin of phenylacetaldehyde,[82] possibly because of isomerization:

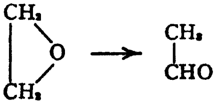


Alkylene cyanohydrins are prepared also by the reaction of olefin oxides with dispersions of the cyanides of alkali or alkaline earth metals in hydroxylic solvents (water, alcohols or mixtures of these).[83] The reaction temperature is maintained between 10° C. and 30° C. The cyanide may be regenerated continuously or intermittently by passing hydrogen cyanide into the solution or suspension of the hydroxide formed.

Isomerization of Olefin Oxides

Besides the above-mentioned purely additive reactions of the olefin oxides, there are also two important reactions of a very different type, namely, isomerization or intramolecular rearrangement, and polymerization. These oxides in the vapor state are isomerized to the corresponding aldehyde or ketone by heat or catalysts or, in the liquid phase, in the presence of hot dilute acids.

When passed through a glass tube at about 500° C., or in the presence of an alumina catalyst at 200° to 300° C., ethylene oxide is converted into acetaldehyde[84]:



The isomerization of ethylene oxide into acetaldehyde in the presence of various catalysts has also been studied by Krassuski,[85] Nef,[86] Peytral,[87] Kaschirsky,[88] and Fourneau and Tiffeneau,[89] and the kinetics of the thermal isomerization in the presence of pyrex glass was investigated by Heckert and Mack.[90]

The reaction is not confined to ethylene oxide as its immediate homologues undergo the reaction more readily. In the presence of alumina at 200° to 300° C., propylene oxide yields mainly propionaldehyde with smaller amounts of acetone; isobutylene oxide, isobutyraldehyde; and trimethylethylene oxide, methyl isopropyl ketone.[91] Dilute mineral acids are active in promoting this isomerization. For instance, dilute sulphuric or sulphurous acids convert methylstyrene oxide into the corresponding aldehyde[92]:

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[82] Fourneau and Tiffeneau, *Compt. rend.*, 1908, **146**, 697; *Chem. Abs.*, 1928, **22**, 1965.

[83] British Patent 348,134, 1930; *Brit. Chem. Abs.* **B**, 1931, 796; French Patent 702,023, 1930; *Chem. Abs.*, 1913, **25**, 4012; British Patent 359,262, 1930; *Chem. Abs.*, 1933, **27**, 309. Fick, German Patent 561,397, 1929; *Chem. Abs.*, 1933, **27**, 998; German Patent 570,031, 1930; *Chem. Abs.*, 1933, **27**, 2458; both patents assigned to I. G. Farbenindustrie A.-G.

[84] Ipatiev and Leontowitsch, *Ber.*, 1903, **36**, 2016.

[85] *J. Russ. Phys.-Chem. Soc.*, 1902, **34**, 537, 556; *Chem. Soc. Abs.*, 1903, **84** (1), 8.

[86] *Ann.*, 1904, **335**, 197.

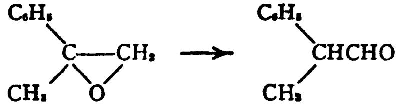
[87] *Bull. soc. chim.*, 1926, **39**, 206; *Chem. Abs.*, 1926, **20**, 1592.

[88] *J. Russ. Phys.-Chem. Soc.*, 1881, **13**, 76; *Chem. Zentr.*, 1881, 279.

[89] *Compt. rend.*, 1905, **140**, 1595; *Chem. Soc. Abs.*, 1905, **88** (1), 591.

[90] *J.A.C.S.*, 1929, **51**, 2706.

[91] Ipatiev and Leontowitsch, *Ber.*, 1903, **36**, 2016.



Isomerization of olefin oxides to aldehydes (or ketones) can be effected by passing them at 180° to 300° C. over a catalyst consisting of magnesium pyrophosphate, copper sulphate or cerous sulphate, with or without the addition of metallic oxides, hydroxides or carbonates, on a carrier.[93] Under these conditions propylene oxide yields propionaldehyde, allyl alcohol and acetone, and the oxides of butene-1 and butene-2, n- and iso-butyraldehydes, methyl ethyl ketone and butenols. Another group of catalysts comprises the halides or oxyhalides of the alkaline earth metals, including magnesium and beryllium.[94]

A mixture of propionaldehyde and allyl alcohol is obtained by conducting propylene oxide vapors, diluted with nitrogen, over activated aluminum at 200° to 400° C.[95]

The passage of 100 parts of ethylene oxide at 220° C. over silica gel impregnated with tungsten oxide at a velocity of 120 to 200 grams per hour per liter of catalyst gives, according to Kathol,[96] 95 to 98 parts of a condensate containing 75 per cent of acetaldehyde, and in addition various by-products such as paraldehyde, crotonaldehyde, dioxan and unsaturated hydrocarbons.

1,2-Oxides derived from cyclic olefins are said to be isomerized to the corresponding ketones by heating in the presence of catalysts such as magnesium sulphate, copper pyrophosphate or silica gel.[97] Thus, menthene-3 oxide yields menthone by heating with 5 per cent silica gel in a closed vessel at 250° C. for two hours. Under similar conditions cyclohexanone is made from cyclohexene oxide.

The isomerization of a number of α-oxides derived from aryl-substituted olefins, including phenyldialkylethylene oxides,[98] styrene oxide,[99] and phenylcyclohexene oxide,[100] has been investigated.

POLYMERIZATION OF OLEFIN OXIDES

Ethylene oxide, and olefin oxides as a class, provide excellent examples of the polymerization of cyclic compounds not involving double bond unsaturation. Treating ethylene oxide with various polymerizing agents such as strong bases (sodium hydroxide, trimethylamine or triethylphosphine) or certain inorganic halides (zinc chloride or tin tetrachloride) produces a profound and highly exothermic condensation.[101] The product is a semi-solid, readily soluble in water and in most organic solvents. It is separable by fractional crystallization into fractions having apparent molecular weights varying from 400 to nearly 5000. The fraction having the lowest molecular weight is a liquid, while the one having the highest is a solid melting at about 59° C. On heating, the polyethylene oxides yield a complex mixture of products containing some acetaldehyde and acrolein.

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[92] Tiffeneau, *Compt. rend.*, 1905, **140**, 1458; *Chem. Soc. Abs.*, 1905, **88** (1), 523.

[93] Baur, German Patent 528,822, 1929; *Chem. Abs.*, 1931, **25**, 5175; British Patent 331,185, 1929; *Brit. Chem. Abs.* **B**, 1930, 939; both patents assigned to I. G. Farbenindustrie A.-G.

[94] Baur, German Patent 535,651, 1930; addition to 528,822; *Chem. Abs.*, 1932, **26**, 994; British Patent 534,388, 1930; *Chem. Abs.*, 1932, **26**, 5310; both patents assigned to I. G. Farbenindustrie A.-G.

[95] Young and Law, Canadian Patent 328,050, 1932; assigned to Carbon and Carbide Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 1012.

[96] German Patent 547,641, 1930; assigned to Rheinische Kampfer Fabrik; *Chem. Abs.*, 1932, **26**, 3521.

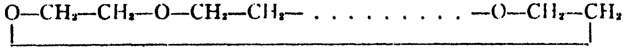
[97] Schering-Kahlbaum A.-G., British Patent 370,823, 1931; *Brit. Chem. Abs.* **B**, 1932, 764; French Patent 723,395, 1931; *Chem. Abs.*, 1932, **26**, 4063.

[98] Lévy and Tabart, *Bull. soc. chim.*, 1931, (4) **49**, 1776; *Chem. Abs.*, 1932, **26**, 2425. See also Tiffeneau and Levy, *Bull. soc. chim.*, 1926, **39**, 763; *Chem. Abs.*, 1926, **20**, 2850.

[99] Lévy and Sfiras, *Bull. soc. chim.*, 1931, (4) **49**, 1823; *Chem. Abs.*, 1932, **26**, 2428. Weill, *Bull. soc. chim.*, 1931, (4) **49**, 1811; *Chem. Abs.*, 1932, **26**, 2427.

[100] Lévy and Sfiras, *Bull. soc. chim.*, 1931, (4) **49**, 1830; *Chem. Abs.*, 1932, **26**, 2428.

It is generally agreed that these polymerized oxides possess a long chain of $—(CH_2CH_2O)—$ residues linked alternately through carbon and oxygen atoms, but the exact configuration of the terminal groups is still uncertain. Roithner[102] assigned the following cyclic structure to the polymerized substances:



$$O—CH_2—CH_2—O—CH_2—CH_2— \ldots\ldots\ldots —O—CH_2—CH_2$$

On the other hand, it appears likely that, in some preparations at least, the terminal groups are hydroxyl groups (due to hydration) and the molecule is thus an open chain.[103]

Wax-like polymerides of olefin oxides are obtained by passing them in the vapor state over alkaline catalysts (sodium or potassium hydroxide) at temperatures from 40° to 200° C.[104] If acid catalysts, e.g., aluminum sulphate or sodium bisulphate, are employed, dioxan and its homologues are formed.

Various technical applications have been suggested for the viscous or solid polymerized olefin oxides. They may be used as ingredients of lacquer and coating compositions in conjunction with cellulose esters,[105] as dispersing agents,[106] as impregnating agents for waxes, resins, rubber, leather or paper,[107] and in the preparation of grounding or priming compositions useful as wood fillers.[108]

HYDROGENATION OF OLEFIN OXIDES

The reduction of olefin oxides, in aqueous solution, to the corresponding alcohols by sodium amalgam has long been known.[109] Alcohols are produced also by vapor-phase catalytic hydrogenation. Ethyl alcohol, for example, is obtained by the reduction of ethylene oxide by an excess of hydrogen at 80° C. under pressure in the presence of a catalyst of nickel on barium oxide. When ethylene oxide is in excess and higher temperatures (130° to 150° C.) are employed, glycol monoethyl ether is formed.[110]

Propylene oxide and hydrogen in the presence of a nickel catalyst at 170° C. yield n-propanol. Butylene oxide similarly gives butyl alcohol, and styrene oxide is converted to phenylethyl alcohol.[111] Propyl alcohol is made also by passing a mixture of propylene oxide and hydrogen (in the molal ratio of about 1:4) and about 10 per cent water vapor first over an aluminum catalyst (at 275° C.) and then over a reduced nickel catalyst (at 150° C.).[112]

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[101] Staudinger and Schweitzer, *Ber.*, 1929, **62**, 2395; Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag von Julius Springer, **1932**, 287.

[102] *Monatsh.*, 1894, **15**, 665; *Chem. Soc. Abs.*, 1895, **68** (1), 319.

[103] Carothers, *Chem. Reviews*, 1931, **8**, 391.

[104] Webel, U. S. Patent 1,921,378, Aug. 8, 1933; *Chem. Abs.*, 1933, **27**, 5082; British Patent 346,550, 1930; *Chem. Abs.*, 1932, **26**, 1941; both patents assigned to I. G. Farbenindustrie A.-G.

[105] I. G. Farbenindustrie A.-G., British Patent 352,042, 1930; *Chem. Abs.*, 1932, **26**, 3391.

[106] I. G. Farbenindustrie A.-G., British Patent 353,926, 1930; *Brit. Chem. Abs.* **B**, 1931, 1132.

[107] I. G. Farbenindustrie A.-G., French Patent 705,852, 1930; *Chem. Abs.*, 1932, **26**, 268; British Patent 349,638, 1930; *Brit. Chem. Abs.* **B**, 1931, 754.

[108] Kollek and Engels, German Patent 529,494, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 5048.

[109] Wurtz, *Ann. chim.*, 1863, (3) **69**, 317, 355. Linnemann, *Monatsh.*, 1865, **6**, 369.

[110] Kathol, German Patent 563,625, 1931; assigned to Rheinische Kampfer-Fabrik G.m.b.H.; *Chem. Abs.*, 1933, **27**, 1012.

[111] Loehr, German Patent 573,535, 1933; *Chem. Abs.*, 1933, **27**, 4240; British Patent 320,424, 1929; *Brit. Chem. Abs.* **B**, 1930, 182; both patents assigned to I. G. Farbenindustrie A.-G.

USES OF ETHYLENE OXIDE

The most important uses of ethylene oxide at present are as a chemical raw material in the preparation of glycol ethers and ethanolamines, and as a fumigant and insecticide. Its application in industrial synthesis has already been mentioned. The use of ethylene oxide as an insecticide was investigated by Cotton and Roark,[113] who reported its vapor to be completely toxic to a number of different kinds of insect pests in stored products at ordinary temperatures in concentrations of 1 to 2 pounds per 1000 cubic feet of space. Ethylene oxide was found to have pronounced powers of penetration with no harmful effects on solid foodstuffs, clothing, furniture, or metals. The comparative toxicity of ethylene oxide and other fumigants was tested by Hoyt,[114] who found that 2 pounds of this compound per 1000 cubic feet of air space were required during a 24-hour exposure at 75° to 80° F. to give a 100 per cent destruction of all the insects used in the test.

Since ethylene oxide is a combustible gas and its extensive use as a fumigant introduces certain hazards of fire and explosion, various means of suppressing these dangers have been investigated. Cotton and Young[115] observed that by mixing carbon dioxide with ethylene oxide the toxicity was considerably increased and the fire hazard reduced or eliminated according to the relative amount of carbon dioxide employed. It was shown by Jones and Kennedy[116] that to render ethylene oxide-air mixtures non-inflammable under all conditions at normal temperatures and pressures at least 7.15 volumes of carbon dioxide per volume of ethylene oxide are required. Further work by Back, Cotton and Ellington[117] indicated the desirability of using at least 7 pounds of carbon dioxide with 1 pound of ethylene oxide. The application of ethylene oxide-carbon dioxide mixtures in fumigation has been discussed by Russ.[118]

In connection with the use of ethylene oxide for the destruction of pests in foodstuffs, Südenorff and Kröger[119] stated that concentrations up to 320 grams per cubic meter have no adverse effect on the quality or flavor of the foods if the space is thoroughly aerated afterwards. According to Thomas,[120] exposure (in enclosed rooms) of infected dried fruits to a concentration of ethylene oxide of 2 pounds per 1000 cubic feet for 4 hours at 20° C. was sufficient to destroy eggs, larvae and pupae.

The use of ethylene oxide mixed with carbon tetrachloride, or other diluents, solvents or irritants, in insecticides was proposed by Taube, Schepss and

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[112] Young and Law, Canadian Patent 328,049, 1932; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 1012.

[113] *Ind. Eng. Chem.*, 1928, **20**, 805; U. S. Patent 1,791,429, Feb. 3, 1931; assigned to the Government and People of the U. S. A.; *Chem. Abs.*, 1931, **25**, 1626. See also Iiams, *Library Quarterly*, 1932, **2**, 375; *Chem. Abs.*, 1933, **27**, 377. Hase, *Arb. biol. Reichanst. Land- u. Forstwirts.*, 1932, **20**, 101; *Brit. Chem. Abs.* **B**, 1933, 286. *Z. Parasitenk.*, 1932, **4**, 369; *Brit. Chem. Abs.* **B**, 1932, 318.

[114] *Ind. Eng. Chem.*, 1928, **20**, 835.

[115] *Proc. Ent. Soc. Washington*, 1929, **31**, 97; *Chem. Abs.*, 1929, **23**, 4523.

[116] *Ind. Eng. Chem.*, 1930, **22**, 146.

[117] *J. Econ. Entom.*, 1930, **23**, 226; *Chem. Abs.*, 1930, **24**, 3610.

[118] *Ind. Eng. Chem.*, 1930, **22**, 328.

[119] *Chem.-Ztg.*, 1931, **55**, 549, 570; *Brit. Chem. Abs.* **B**, 1931, 904.

[120] *J. Council Sci. Ind. Res., Australia.* 1931, **4**, 53; *Chem. Abs.*, 1931, **25**, 3095. See also Morgan, *Food Tech.*, 1932, **1**, 213; *Brit. Chem. Abs.* **B**, 1932, 369; Lindgreen and Shepherd, *J. Econ. Entom.*, 1932, **25**, 248; *Brit. Chem. Abs.* **B**, 1932, 570.

Kükenthal.[121] Germicidal and insecticidal preparations containing mixtures of ethylene and propylene oxides, carbon disulphide, or vinyl chloride with inert gases (nitrogen or carbon dioxide) in sufficient quantity to render the mixture non-inflammable, were suggested by the T. Goldschmidt A.-G.[122] A bactericide (formaldehyde) can also be added.[123] Solidified mixtures of ethylene oxide and carbon dioxide are stated to be vermin-destroying compositions.[124]

Although it has been repeatedly stated that ethylene oxide is relatively non-toxic to man, experimental evidence seems to indicate that it possesses decidedly toxic properties and that certain precautions are necessary when fumigating with it. Koelsch and Leder[125] studied the toxic action of ethylene oxide on animals at concentrations of 1 : 50 to 1 : 10,000 in air and found that severe and sometimes fatal symptoms were induced. Particularly noticeable were the diminution in weight due to changes in metabolism, with narcosis, coma and paralysis of the limbs. The toxicity of ethylene oxide was noted also by Walker and Greeson.[126] In experiments on cats exposed to various concentrations of ethylene oxide vapors, Müller[127] observed an initial stimulation of the nasal mucosa resulting in watering of the eyes, sneezing, licking of the lips and leading to difficult respiration, vomiting, and finally to death. He concluded that the accidental exposure of man to concentrations of 32 grams of ethylene oxide per cubic meter need not be feared, but thorough ventilation of rooms, after fumigation, is essential.[128]

Ethylene oxide mixed with low-boiling liquids, such as methyl ethyl ether and propane, can be used for the de-waxing of petroleum distillates.[129] The oil is added to the solvent in the liquid phase under pressure and the mixture cooled to —23° C. by self-evaporation of some of the solvent. The precipitated wax is removed by filtration. The liquid oxide, mixed with some methyl alcohol, has been suggested as a fuel for certain types of portable cigarette lighters.[130] Nitroglycerol, glycol dinitrate, cellulose nitrate and other organic nitrates can be stabilized by treatment with ethylene oxide.[130a]

DETECTION OF ETHYLENE OXIDE

Deckert[131] suggested the following method for detecting ethylene oxide in air. Two hundred cubic centimeters of air are drawn through 5 cc. of a 22 per cent sodium chloride solution which contains either phenolphthalein or bromothymol blue as an indicator. The solution is then heated for 1 minute at 100° C. If there is no color change the concentration of the oxide in air was less than

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[121] German Patent 507,215, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 554. Also British Patent 308,661, 1928; *Chem. Abs.*, 1930, **24**, 458; and German Patents 556,913 and 556,914, 1928; *Chem. Abs.*, 1933, **27**, 805. *Cf.* Marx and Brodersen, German Patent 511,544, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 1326.

[122] British Patent 318,898, 1928; *Chem. Abs.*, 1930, **24**, 2539; British Patent 377,552, 1930; *Chem. Abs.*, 1933, **27**, 2754; German Patent 568,591, 1930; *Chem. Abs.*, 1933, **27**, 2754; German Patent 514,775, 1928; *Chem. Abs.*, 1931, **25**, 4352; German Patent 543,307, 1930; *Chem. Abs.*, 1932, **26**, 3324.

[123] T. Goldschmidt A.-G., German Patent 552,034, 1930; *Chem. Abs.*, 1932, **26**, 6083.

[124] Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, British Patent 353,354, 1930; *Brit. Chem. Abs.* **B**, 1931, 908.

[125] *Zentr. Gewerbehyg. Unfallverhütung*, 1930, **17**, 264; *Chem. Abs.*, 1931, **25**, 4059.

[126] *J. Hyg.*, 1932, **32**, 409; *Chem. Abs.*, 1932, **26**, 5345.

[127] *Z. Desinfekt. Gesundh.*, 1931, 178; *Ar. Reichsegesundh.*, 1931, **64**, (1), 83; *Chem. Abs.*, 1932, **26**, 1063.

[128] The destructive action of ethylene oxide on various plants and shrubs when injected into the soil at the roots has been noted by Harvey, *Science*, 1931, **73**, 100; *Chem. Abs.*, 1931, **25**, 4082; *Phytopath.*, 1931, **21**, 126; *Brit. Chem. Abs.* **B**, 1931, 1150.

[129] Vorhees, U. S. Patent 1,862,874, June 14, 1932; assigned to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, **26**, 4168.

[130] Fisher, U. S. Patent 1,895,032, June 24, 1933; *Chem. Abs.*, 1933, **27**, 2559.

[130a] Werntz, U. S. Patent 1,846,926, Feb. 23, 1932; assigned to E. I. duPont de Nemours & Co., Inc.; *Chem. Abs.*, 1932, **26**, 2468.

[131] *Z. angew. Chem.*, 1932, **45**, 559; *Chem. Abs.*, 1932, **26**, 5877.

0.5 mg. per liter (phenolphthalein) or less than 0.1 mg. (bromothymol blue), and the air is safe.

Another test consists in passing 50 cc. of air through 1 or 2 cc. of a 40 per cent potassium sulphocyanide solution to which is added 1 cc. of a phenolphthalein solution (1:1000). If a red color does not appear after warming the test tube (holding it in the hand) for 2 minutes, the air is free of ethylene oxide.[182]

A quantitative determination, suggested by Deckert,[183] is based on the reaction between ethylene oxide and hydrochloric acid:

$$C_2H_4O + HCl \longrightarrow CH_2ClCH_2OH$$

A measured volume of air is led through 0.1*N* hydrochloric acid, containing 22 per cent of sodium chloride. The solution is heated to 70° C. to convert all the oxide into ethylene chlorohydrin. The excess hydrochloric acid is titrated with 0.1*N* sodium hydroxide, using methyl-orange as an indicator. Each cc. of 0.1*N* hydrochloric acid reacting represents 4.4 mg. of ethylene oxide.

Lubatti[184] reported that Deckert's method accounts for about 90 per cent of the ethylene oxide present in the air. He recommends that more soluble chlorides, particularly magnesium chloride, be substituted for sodium chloride. Furthermore, the chloride solution should contain the equivalent of at least 30 grams of chlorine per 100 cc.

The estimation of ethylene oxide by oxidation to carbon dioxide and water with potassium dichromate and sulphuric acid was described by Müller.[185]

ETHANOLAMINES

As previously stated in this chapter, the combination of aqueous ammonia with ethylene oxide results in the formation of a mixture of three basic substances which may be separated by distillation. The proportions of the three products depend largely on the relative proportions of the reactants, an excess of ethylene oxide favoring the formation of triethanolamine.[186] The three bases, and particularly their mixtures, are assuming a position of importance in chemical industry.

In the method of production described by Reid and Lewis,[187] ammonia and ethylene oxide are brought into reaction by passing a stream of a solution of one of the reacting substances at a temperature below 50° C. along a porous wall and diffusing the other reactant through the wall. In another procedure, the olefin oxide is added to an aqueous solution of ammonia.[188] Thus, 2600 parts of ethylene oxide are added slowly to 3870 parts of 25 per cent aqueous ammonia at 25° to 30° C. to give 90 to 95 per cent yield of triethanolamine. If 352 parts of ethylene oxide are added to 3400 parts of 25 per cent ammonia solution at 10° C., monoethanolamine is formed almost exclusively.[189]

[182] Deckert, *Z. angew. Chem.*, 1932, 45, 758; *Chem. Abs.*, 1933, 27, 685.

[183] *Z. anal. Chem.*, 1930, 82, 297; *Brit. Chem. Abs.* B, 1931, 180. Deckert suggested the following reactions:

$$C_2H_4O + NaCl + H_2O \rightarrow CH_2ClCH_2OH + NaOH$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$

[184] *J.S.C.I.*, 1932, 51, 361T.

[185] *Chem.-Ztg.*, 1920, 44, 513; *Chem. Soc. Abs.*, 1920, 118 (2), 515.

[186] Knorr, *Ber.*, 1897, 30, 909. Germann and Knight (*J.A.C.S.*, 1933, 55, 4150) described the preparation of pure triethanolamine.

[187] Canadian Patent 298,851, 1930; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1930, 24, 2756.

[188] I. G. Farbenindustrie A.-G., French Patent 650,574, 1929; *Chem. Abs.*, 1929, 23, 3232; British Patent 306,563, 1927; *Brit. Chem. Abs.* B, 1929, 315. Also Reid and Lewis, U. S. Patent 1,904,013, April 18, 1933; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, 27, 3222.

[189] Cyclohexylethanolamines are similarly made from cyclohexylamine and ethylene oxide, I. G. Farbenindustrie A.-G., German Patent 535,049, 1927; *Chem. Abs.*, 1932, 26, 995.

Arnold[139a] formed secondary and tertiary amines by passing alcohol and ammonia in the proportions of 3 to 4 parts alcohol to 1 part ammonia over a catalyst (alumina or thoria), 85 per cent of the ammonia being converted.

The boiling points of the three bases are as follows:

Monoethanolamine, $NH_2CH_2CH_2OH$, 171° C. at 757 mm.
Diethanolamine, $NH(CH_2CH_2OH)_2$, 217° C. at 150 mm.
Triethanolamine, $N(CH_2CH_2OH)_3$, 277° C. at 150 mm.

The three ethanolamines differ slightly in their chemical and physical properties. They are miscible in all proportions with water, the ordinary alcohols, acetone, glycerol and ethylene chlorohydrin but not with diethyl ether and some aldehydes. The salts with the higher fatty acids are emulsifying agents and soaps.

Monoethanolamine is a colorless, slightly viscous, very highly hygroscopic liquid with a faint but agreeable ammoniacal odor. The dinitrate of this compound may be prepared by dissolving the ethanolamine in excess nitric acid, distilling off the excess *in vacuo* and precipitating the dinitrate by pouring it into cold alcohol or alcohol-ether mixture.[140] The yield is said to be 88 to 97 per cent. The dinitrate has been proposed as an explosive either alone or mixed with other substances.

Diethanolamine is a colorless and odorless liquid having a viscosity like that of glycerol. Diethanolamine trinitrate has been proposed as an explosive.[141]

Triethanolamine, when pure, is a white crystalline solid at room temperatures. Commercial triethanolamine is a clear, viscous, and very hygroscopic liquid of d^{20}_{4} 1.124, soluble in most organic liquids containing oxygen, but only slightly soluble in hydrocarbons. Despite its feeble alkalinity (dissociation constant, 2.5×10^{-6}), stable salts are formed with most acids although its abietic acid salt is almost completely hydrolyzed in aqueous solution.

APPLICATIONS OF THE ETHANOLAMINES

Mixtures of the ethanolamines may be used in the purification of gases from carbon dioxide and hydrogen sulphide. A 50 per cent aqueous solution of a mixture of di- and tri-ethanolamines is employed for absorbing these acidic gases by countercurrent washing at room temperature. The resulting solution of the acid sulphides or carbonates of the ethanolamines readily decomposes at temperatures above 50° C. with regeneration of the absorbent.[142] A 50 per cent aqueous solution of triethanolamine ("Girbotol") will absorb 6.7 cu. ft. of carbon dioxide (measured under standard conditions) per gallon under a pressure of 760 mm. of mercury at 95° F.[143] The advantages of the ethanolamines in gas purification are: less liquid is required for a given quantity of carbon dioxide than with sodium carbonate; the vapor pressures of the absorbents are low enough to obviate loss of material by evaporation; and corrosion troubles are not encountered. The ethanolamines form more stable salts with sulphur dioxide, and hence are unsuitable for the removal of this substance from gases.

[139a] U. S. Patent 1,799,722, April 7, 1931; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1931, **25**, 3012; Canadian Patent 315,874, 1931; assigned to The Canadian Industries, Ltd.; *Chem. Abs.*, 1932, **26**, 1297.

[140] Naoúm and von Sommerfeld, German Patent 514,955, 1929; *Chem. Abs.*, 1931, **25**, 2739; German Patent 516,284, 1929; *Chem. Abs.*, 1931, **25**, 3362; German Patent 517,832, 1930; *Chem. Abs.*, 1931, **25**, 2740; all patents assigned to Dynamit A.-G. vorm. Alfred Nobel and Co.

[141] Dynamit A.-G. vorm. Alfred Nobel and Co., French Patent 696,632, 1930; *Chem. Abs.*, 1931, **25**, 2853. Naoúm and Ulrich, German Patent 500,407, 1929; *Chem. Abs.*, 1930, **24**, 4397; assigned to Dynamit A.-G. vorm. Alfred Nobel and Co.

[142] Bottoms, U. S. Patent 1,783,901, Dec. 2, 1930; assigned to The Girdler Corp.; *Ind. Eng. Chem.*, 1931, **23**, 501; *Proc. Amer. Gas Assoc.*, 1931, **13**, 1071; *Chem. Abs.*, 1932, **26**, 4157; *Chem. Met. Eng.*, 1931, **38**, 465. The Girdler Corp., British Patent 344,786, 1928; *Chem. Abs.*, 1931, **25**, 4671; French Patent 685,992, 1929; *Chem. Abs.*, 1930, **24**, 5898. See also Albright, *Refiner*, 1932, **11** (1), 19; *Chem. Abs.*, 1932, **26**, 3090; Garrison, *Proc. Amer. Gas Assoc.*, 1931, **13**, 1056; *Chem. Abs.*, 1932, **26**, 5403.

[143] Lamberth, *Oil and Gas J.*, 1932, **30** (45), 18. Also Mayer, *Allgem. österr. Chem.- u. Tech.-Ztg.*, 1931, **49** (9), 43; *Chem. Abs.*, 1931, **25**, 3814.

Stanier[144] suggested using the ethanolamines for extracting phenols from tar oils. The ethanolamine extract is diluted with water and then saturated with carbon dioxide or hydrogen sulphide to recover the phenols. Ethanolamines have been proposed as extraction agents for the refining of mineral oils.[145] The addition of a small proportion (0.05 to 1.0 per cent) of butyldiethanolamine to lubricating oils stabilizes their color.[146]

The ethanolamines have also been applied in the preparation of photographic films,[147] and of wetting agents,[148] as plasticizers with cellulose esters,[149] as soaking and softening agents for hides and pelts,[150] and as catalysts in the formation of phenol-aldehyde condensation products.[151] These amines have served as preservative agents in rubber compositions,[152] as stabilizers for lead tetra-alkyls,[153] as inhibitors of iron corrosion by methyl and ethyl alcohols, glycol, or glycerol,[154] for the dehydration of acetic acid,[155] and in conjunction with boric acid or rosin for the electrolytic deposition of solid films of high dielectric strength.[156] Dissolved in water or alcohol[156a] or in the form of their borates[157] the ethanolamines are of therapeutic value.

Any one of the ethanolamines, as well as the technical mixture, combines readily with fatty acids to produce soaps,[158] whose consistency depends more upon the fatty acid employed than upon the particular ethanolamine. Monoethanolamine oleate has the consistency of petroleum jelly and the oleates of the other ethanolamines are only slightly less viscid. The stearate is a hard, wax-like solid. These soaps are soluble in water, the usual organic solvents (benzene, toluene, turpentine) and to a limited extent in lubricating and petroleum oils. Ethanolamine oleate possesses frothing and emulsifying properties and may be used for promoting oil-in-water emulsions.

Among the many proposed applications for ethanolamine soaps the following may be mentioned: as a flux in soft soldering,[159] for increasing the electrical conductivity of light petroleum distillates[160] (to minimize danger of sparking and explosion when cleaning with these materials), as ingredients for spray compositions for agricultural purposes,[161] in the preparation of sizes[162] and greasing agents[163] for textile fibers, and in the degumming of silk.[164]

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[144] British Patent 344,614, 1931; assigned to South Metropolitan Gas Co.; *Brit. Chem. Abs.* **B**, 1931, 528.

[145] Rosenstein and Hund, British Patent 391,658, 1932; *Brit. Chem. Abs.* **B**, 1933, 555. Dietrich, U. S. Patent 1,882,002, Oct. 11, 1932; assigned to DeLaval Separator Co.; *Chem. Abs.*, 1933, **27**, 594.

[146] Adams, U. S. Patent 1,888,023, Nov. 15, 1932; assigned to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, **27**, 1502.

[147] Kodak-Pathé, French Patent 732,933, 1932; *Chem. Abs.*, 1933, **27**, 240.

[148] Frederic Steinfels (Soc. Anon.) Fabrique de Savons Zurich, French Patent 717,031, 1931; *Chem. Abs.*, 1932, **26**, 2834. I. G. Farbenindustrie A.-G., French Patent 715,756, 1931; *Chem. Abs.*, 1932, **26**, 2026; Somerville, U. S. Patent 1,836,047, Dec. 15, 1931; assigned to Röhm and Haas Co.; *Chem. Abs.*, 1932, **26**, 1403.

[149] Staud and Webber, U. S. Patent 1,880,514, Oct. 4, 1932; assigned to Eastman Kodak Co.; *Chem. Abs.*, 1933, **27**, 601.

[150] I. G. Farbenindustrie A.-G., British Patent 341,851, 1929; *Chem. Abs.*, 1933, **27**, 625.

[151] Cameron and Jackson, British Patent 364,304, 1929; assigned to The British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, **27**, 1774.

[152] Twiss and Jones, British Patent 389,637, 1932; assigned to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs.* **B**, 1933, 437.

[153] Calcott and Parmelee, U. S. Patent 1,843,942, Feb. 9, 1932; assigned to E. I. duPont de Nemours and Co., Inc.; *Brit. Chem. Abs.* **B**, 1933, 296.

[154] Calcott and Walker, U. S. Patent 1,847,711, March 1, 1932; assigned to E. I. duPont de Nemours and Co., Inc.; *Brit. Chem. Abs.* **B**, 1933, 53.

[155] Othmer, U. S. Patent 1,897,816, Feb. 14, 1933; assigned to Eastman Kodak Co.; *Chem. Abs.*, 1933, **27**, 2695.

[156] Samuel, British Patent 387,437, 1931; *Brit. Chem. Abs.* **B**, 1933, 313.

[156a] Graves, U. S. Patent 1,913,631, June 13, 1933; *Chem. Abs.*, 1933, **27**, 4351.

[157] Rojahn, German Patent 582,149, 1933; *Chem. Abs.*, 1933, **27**, 5153.

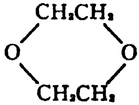
[158] Trusler, *Ind. Eng. Chem.*, 1931, **21**, 685. See also Trusler, *Soap*, 1929, **4** (7), 33; *Chem. Abs.*, 1929, **23**, 2588. An account of the industrial applications of ethanolamine soaps is given by Smith, *Soap*, 1931, **7** (12), 27; *Chem. Abs.*, 1932, **26**, 866. For the use of ethanolamine soaps as detergents see Moscowitz, U. S. Patent 1,847,437, March 1, 1932; *Chem. Abs.*, 1932, **26**, 2613; Hoyt, U. S. Patent 1,833,899, Dec. 1, 1931; assigned to Larkin Co.; *Chem. Abs.*, 1932, **26**, 1147. Kruege (*Seifensieder-Ztg.*, 1933, **60**, 310; *Chem. Abs.*, 1933, **27**, 5206) describes the preparation of a triethanolamine ricinoleate soap.

Monoethanolamine oleate has been suggested as a component of cleaning and polishing mixtures,[165] and the soaps of triethanolamine and oleic acid, or high molecular weight carboxylic or sulphonic acids, may be used as auxiliary agents (disinfectants or lubricants) in the textile, leather and paper industries.[166]

The various soaps of triethanolamine (particularly the oleate and the linoleate) are useful for emulsifying[166a] and other purposes. The oleate is a viscous soap completely miscible with many organic liquids including hydrocarbons, except certain heavy mineral oils and fatty glycerides which may require the addition of an excess of acid to yield a clear solution. The use of triethanolamine soaps for emulsification purposes has been discussed by Wilson.[167] Combinations of triethanolamine with fatty acids, oils, and solvents to be employed as detergents, lubricants, and dry cleaning compounds were described by Harvey.[168] The preparation of various water emulsions for orchard-spraying purposes was given by Hockenyos.[169]

The salts of triethanolamine with oil-soluble sulphonic acids[170] or with sulphonated castor or fish oils[171] are said to be detergents, and the resinates or naphthenates have been proposed as sizes for textile threads.[172] Other uses for the triethanolamine soaps are as dispersing agents for dyes[173] and in the preparation of wick fibers.[174]

DIOXAN (DIETHYLENE DIOXIDE)

The close structural relationship of dioxan, , and the olefin oxides renders a description of this substance appropriate at this stage.

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[159] McQuaid, U. S. Patents 1,785,134 and 1,785,135, Dec. 16, 1930; assigned to Grasselli Chemical Co.; *Chem. Abs.*, 1931, **25**, 484.

[160] Kritchevsky and Morrill, U. S. Patent 1,810,660, June 16, 1931; *Chem. Abs.*, 1931, **25**, 4697; Canadian Patent 309,989, 1031; *Chem. Abs.*, 1931, **25**, 3157; both patents assigned to Sparkless Cleaner Co. For reduction of electrification of artificial sheets, films or foils, see Dreyfus, British Patent 387,710, 1931; *Brit. Chem. Abs.* **B**, 1933, 302.

[161] Linstaedt, Canadian Patent 307,169, 1930; *Chem. Abs.*, 1931, **25**, 767; U. S. Patent 1,890,158, Dec. 6, 1932; *Chem. Abs.*, 1933, **27**, 1709; both patents assigned to Hercules Glue Co.

[162] Étab. Gamma, British Patent 364,902, 1931; *Brit. Chem. Abs.* **B**, 1932, 304. Bianchini Ferier (Soc. en nom collectif), French Patent 40,532, 1930, addition to 615,134; *Chem. Abs.*, 1933, **27**, 1523. I. G. Farbenindustrie A.-G., French Patent 41,447, 1932, addition to 669,517; *Chem. Abs.*, 1933, **27**, 2774.

[163] I. G. Farbenindustrie A.-G., French Patent 705,405, 1930; *Chem. Abs.*, 1921, **25**, 5300.

[164] Harvey, U. S. Patent 1,828,736, Oct. 27, 1931; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1932, **26**, 857.

[165] Bennett, U. S. Patent 1,807,563, May 26, 1931; *Chem. Abs.*, 1931, **25**, 4142.

[166] I. G. Farbenindustrie A.-G., French Patent 710,415, 1931; *Chem. Abs.*, 1932, **26**, 1716.

[166a] For a review of triethanolamine emulsions see Navarre, *Am. Perfumer*, 1933, **27**, 650; *Chem. Abs.*, 1933, **27**, 1713.

[167] *Ind. Eng. Chem.*, 1930, **22**, 143.

[168] *Proc. Am. Assoc. Textile Chem. Colorists*, 1930, **24**, 101; *Amer. Dyestuffs Reptr.*, 1930, **19**, 185; *Chem. Abs.*, 1930, **24**, 3377.

[169] *Ind. Eng. Chem.*, 1929, **21**, 647.

[170] Reddish, U. S. Patent 1,780,144, Oct. 28, 1930; assigned to The Twitchell Process Co.; *Brit. Chem. Abs.* **B**. 1931, 667.

[171] Wall, U. S. Patent 1,812,615, June 30, 1931; assigned to Kali Manufacturing Co.; *Chem. Abs.*, 1931, **25**, 4954.

[172] Kousnetzoff, British Patent 363,448, 1930; *Brit. Chem. Abs.* **B**, 1932, 258; French Patent 709,431, 1930; *Chem. Abs.*, 1932, **26**, 1455. Dreyfus, French Patent 741,369, 1932; *Chem. Abs.*, 1933, **27**, 2773.

[173] I. G. Farbenindustrie A.-G., British Patent 368,746, 1930; *Brit. Chem. Abs.* **B**, 1932, 671. Basch, French Patent 738,950, 1932; *Chem. Abs.*, 1933, **27**, 1995.

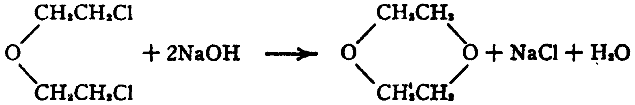
[174] Dreyfus, French Patents 741,405 and 741,406, 1932; *Chem. Abs.*, 1933, **27**, 2825.

Dioxan is made in a number of ways, among which the following may be mentioned:

(1) By heating ethylene bromide with ethylene glycol.[175]

(2) By the combination of ethylene oxide and ethylene chlorohydrin.[176] Other products, however, are formed at the same time.

(3) By the action of sodium hydroxide on $\beta\beta'$-dichlorodiethyl ether,[177] according to the reaction:



A 22 per cent yield of dioxan is obtained, the other product being β-chloroethyl vinyl ether. Heating $\beta\beta'$-dichloroethyl ether with metallic oxides, e.g., mercuric, lead, silver or cupric oxides, has been suggested.[178]

(4) By the action of dehydrating agents (for example, phosphoric acid) on ethylene glycol or by heating ethylene oxide with sodium hydroxide.[179]

The method of preparation, which is also employed industrially, is that originally proposed by Faworski,[180] who obtained dioxan together with some ethyl acetal by distilling glycol with 4 per cent of sulphuric acid. Distillation of diethylene glycol (dihydroxydiethyl oxide) or a monoether derivative with sulphuric acid also yields dioxan.[181] Van Alphen[182] described a method of converting ethylene glycol into dioxan by heating it with anhydrous ferric sulphate, a procedure appearing to give good results. Mixtures of dioxan homologues may be obtained by treating mixtures of glycols with dehydrating catalysts.[183] For example, twenty-five parts of olefin glycols (made from cracking gas) and 1 part of concentrated sulphuric acid are heated to boiling in an acid-resisting distilling vessel, further amounts of the glycol mixture being added in amount corresponding to the quantity of dioxans distilling off. The yield of mixed dioxans, boiling point 95° to 150° C., was 80 per cent of the theoretical. On distilling 25 parts of propylene glycol and 1 part of concentrated sulphuric acid in the manner previously described, an 80 per cent yield of dimethyldioxan was obtained. A similar yield of diethyldioxan may be had from 1,2-butylene glycol in the same manner. High molecular weight polyglycols or polymers of alkylene oxides, when distilled in the presence of a dehydrating catalyst, are also said to yield dioxan and its homologues.[183a]

PROPERTIES OF DIOXAN

Dioxan is a liquid of faint odor, boiling at 102° C., melting at 11° C. and d_4^{20} 1.0329. Its heat of fusion is 33.8 calories per gram and molal heat of combustion, 554.6 calories.[184] It is soluble in water and in many organic solvents and is a fair solvent for resins and fats. It has been suggested as a solvent for cellulose esters[185] and also for the hydrolysis of cellulose acetate.[186] The technical product usually contains some ethylene acetal as well as a peroxide probably derived from the latter. Both these substances can be removed by boiling the crude dioxan with one-tenth its volume of normal hydrochloric acid for several hours.[187] Dioxan can be used for the extraction of lithium chloride from mixtures with the chlorides of sodium and potassium.[188]

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[175] Lourenço, *Ann. chim.*, 1863, (3) **64**, 275.

[176] Fourneau and Ribas, *Bull. soc. chim.*, 1927, (4) **41**, 1046.

[177] Cretcher, Koch and Pittenger. *J.A.C.S.*, 1925, **47**, 1173. Reid, U. S. Patent 1,879,637, Sept. 27, 1932; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 313. See also British Patent 363,895, 1930; *Brit. Chem. Abs.* **B**, 1932, 378; French Patent 711,595, 1931; *Chem. Abs.*, 1932, **26**, 1947. Webel, German Patent 526,478, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 737.

[178] Dreyfus, British Patent 374,134, 1931; *Brit. Chem. Abs.* **B**, 1932, 832.

[179] Davidson, *Ind. Eng. Chem.*, 1926, **18**, 669; *cf.* Knorr, German Patent 500,223, 1924; *Chem. Abs.*, 1930, **24**, 4307; German Patent 516,844, 1927; *Chem. Abs.*, 1931, **25**, 1841; both patents assigned to I. G. Farbenindustrie A.-G.

[180] *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 741; *Chem. Zentr.*, 1907, 1, 15. This method appears to be a fairly general one for the production of dioxan homologues. Thus, phenylglycol on heating with 4 per cent sulphuric acid yields the corresponding dimolecular ether. (Breuer and Zincke, *Ber.*, 1878, 11, 1402.)

[181] I. G. Farbenindustrie A.-G., German Patent 507,761, 1926; *Chem. Abs.*, 1931, **25**, 524.

[182] *Rec. trav. chim.*, 1930, **49**, 1040; *Chem. Abs.*, 1931, **25**, 75.

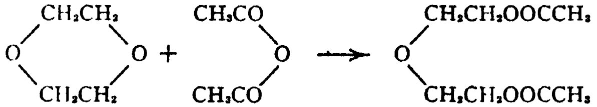
[183] I. G. Farbenindustrie A.-G., British Patent 318,758, 1929; *Brit. Chem. Abs.* **B**, 1929, 973.

[183a] I. G. Farbenindustrie A.-G., German Patent 570,674, 1933; *Chem. Abs.*, 1933, **27**, 4252.

The explosive properties of dioxan-air mixtures were studied by Jones, Seaman and Kennedy.[188a] The lower inflammable limit of dry dioxan-air mixtures at room temperatures and pressures was 1.97 per cent by volume. The upper limit at atmospheric pressure and temperatures of 100° to 110° C. was found to be 22.25 per cent by volume.

From a purely chemical standpoint dioxan is of interest because of the ease with which it forms crystalline double compounds with halogens, metallic chlorides and other reagents. Of these the dibromide, m.p. 65°-66° C., and the diiodide, m.p. 84°-85° C., are characteristic.[189] With sulphuric acid it forms a compound of the formula, $C_4H_8O_2.H_2SO_4$, which may be crystallized from benzene and which melts at 101° C. With nitric acid in the cold it yields the addition product of the formula $3C_4H_8O_2.4HNO_3$, which melts at 14° C.[190] Double compounds with stannic chloride have also been described.[191]

Acetylation of dioxan with acetic anhydride in the presence of anhydrous ferric chloride yields small quantities of glycol diacetate together with $\beta\beta'$-diacetoxydiethyl ether[192] (diethylene glycol diacetate), boiling at 110° to 135° C. at 16 mm.



Direct chlorination of dioxan at 90° C. produces 2,3-dichlorodioxan,[193] and ultimately, of several isomeric tetrachlorodioxanes.[194]

Dioxolanes. Bogert and Roblin[194a] prepared a series of cyclic acetals (1,3-dioxolanes) in yields of 25 to 35 per cent by the reaction of ethylene oxide with aldehydes and ketones in the presence of anhydrous stannic chloride. The properties of these compounds are given in Table 107.

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[184] Roth and Meyer, *Z. Elektrochem.*, 1933, **39**, 35; *Chem. Abs.*, 1933, **27**, 1566.

[185] Knorr, German Patent 431,249, 1925; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1927, 249. Also British Patent 275,653, 1925; *Brit. Chem. Abs.* **B**, 1927, 905. Dimethyl- or diethyl-dioxan together with ethyl and butyl alcohols have been suggested by Jordan (U. S. Patent 1,919,727, July 25, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4943) as solvents for cellulose derivatives.

[186] Webber and Staud, U. S. Patent 1,826,335, Oct. 6, 1931; assigned to Eastman Kodak Co.; *Chem. Abs.*, 1932, **26**, 598.

[187] Eigenberger, *J. prakt. Chem.*, 1931, **130**, 75; *Chem. Abs.*, 1931, **25**, 3315.

[188] Sinka, *Z. anal. Chem.*, 1930, **80**, 430; *Brit. Chem. Abs.* **A**, 1930, 1146.

[188a] *Ind. Eng. Chem.*, 1933, **25**, 1283.

[189] Wurtz, *Ann. chim.*, 1863, (3) **69**, 321. Paternò and Spallino, *Atti accad. Lincei*, 1907, (5) 16, 1, 87; *Chem. Soc. Abs.*, 1907, **92** (1), 274. Rheinboldt and Boy, *J. prakt. Chem.*, 1931, **129**, 273; *Chem. Abs.*, 1931, **25**, 2691.

[190] Van Alphen, *Rec. trav. chim.*, 1930, **49**, 1040; *Chem. Abs.*, 1931, **25**, 75.

[191] Rheinboldt and Boy, *J. prakt. Chem.*, 1931, **129**, 268; *Chem. Abs.*, 1931, **25**, 2691.

[192] Macleod, *J.C.S.*, 1928, 3092.

[193] Böeseken, Tellegen and Henriques, *Proc. Roy. Soc. Amsterdam*, 1931, **34**, 631; *Chem. Abs.*, 1931, **25**, 5170; *Rec. trav. chim.*, 1931, **50**, 909; *Chem. Abs.*, 1931, **25**, 4849.

[194] Butler and Cretcher, *J.A.C.S.*, 1932, **54**, 2987.

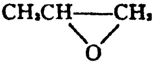
[194a] *J.A.C.S.*, 1933, **55**, 3741.

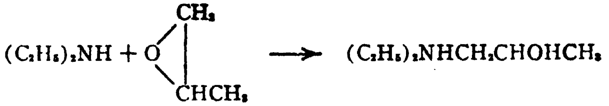
TABLE 107.—*Properties of Dioxolanes.*

Compound	Boiling Point at 23 mm. °C.
4-Methyl-2-phenyl-1,3-dioxolane	118
4-Methyl-2-hexyl-1,3-dioxolane	102.5–103.5
2-Methyl-2-hexyl-1,3-dioxolane	97
2,4-Dimethyl-2-hexyl-1,3-dioxolane	102
2-Methyl-2-phenyl-1,3-dioxolane	103.5–104.5 (melting point 62)
2,4-Dimethyl-2-phenyl-1,3-dioxolane	105

HOMOLOGUES OF ETHYLENE OXIDE

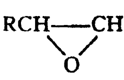
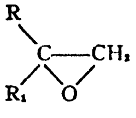
Of the higher olefin oxides only propylene oxide will be considered in any detail since the properties of the higher oxides have been little investigated.

Propylene oxide,  , is a liquid, boiling point 35° C., which may be prepared by methods analogous to those for ethylene oxide. In chemical properties it is very similar to ethylene oxide though its reactivity is somewhat less.[195] It can be hydrated to propylene glycol and reduced to n-propanol. It reacts with alcohols and phenols to yield monoethers of propylene glycol, and with organic acids to form esters of this glycol. Like ethylene glycol it reacts with ammonia and amines. Thus, 1 mole of this oxide when heated with 2 moles of diethylamine in aqueous solutions (of either 33 or 70 per cent concentrations of amine), gives 65 per cent of 3-diethylaminopropanol-2, a liquid boiling at 158° to 159° C. (760 mm.).[196]



Similarly, propylene oxide condenses with benzylamine at 100° C. to yield 1-benzylamino-2-propanol and with isoamylamine to give 1-isoamylamino-2-propanol.[197] The presence of water accelerates these combinations and increases the yields.

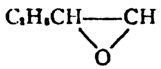
Propylene oxide, like other oxides of the type,

 and 

contains an asymmetric carbon atom and therefore exhibits stereoisomerism.

BUTENE OXIDES

Three α-oxides of the butene series are known, namely:

1,2-Butene oxide,  boiling point 58.5°–58.9° C.

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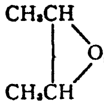
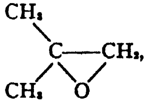
[195] Boyd and Marle, *J.C.S.*, 1914, 105, 2117.
[196] Krassuski and Pilyugin, *Ukrainskii Khem. Zhur.*, 1930, 5, 135; *Chem. Abs.*, 1931, 25, 2690.
[197] Krassuski and Pilyugin, *Ukrainskii Khem. Zhur.*, 1930, 5, Sci. Part, 237; *Chem. Abs.*, 1931, 25, 3632.

2,3-Butene oxide,



boiling point 56°-57° C.

Isobutene oxide,

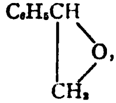


boiling point 51°-52° C.

Isobutene oxide is remarkable on account of the ease of combination with water, a reaction which takes place at ordinary temperatures with the evolution of heat.[198] It reacts with ammonia to yield aminotrimethylcarbinol as well as large amounts of secondary and smaller amounts of tertiary amines.[199]

The number of the isomers of the olefin oxides increases greatly with increasing molecular weight. Little is known of these higher oxides and they are of little industrial significance. Of the pentene oxides, isopropylethylene oxide is hydrated to the corresponding glycol with difficulty. Its reactions with ethylamine and diethylamine have been investigated by Krivonos.[200]

Styrene oxide,



is an interesting aryl-substituted olefin oxide which could be produced in quantity if an industrial application of it were discovered. This oxide is prepared from crude styrene chlorohydrin which generally contains some of the corresponding dichloride.[201] The crude chlorohydrin is decomposed with aqueous potassium hydroxide to yield 90 per cent of the oxide (b.p. 70° C. under 5 mm. pressure) and the styrene dichloride is recovered unchanged. Styrene oxide is remarkable for the ease with which it isomerizes to phenylacetaldehyde in the presence of dilute acids.[202] It readily combines with hydrogen cyanide to give the cyanohydrin of phenylacetaldehyde.

[198] Eltekov, *J. Russ. Phys.-Chem. Soc.*, 1882, 14, 355; *Ber.*, 1883, 16, Ref. 395; *Chem. Soc. Abs.*, 1883, 44, 566.

[199] Krassuski and Duda, *J. prakt. Chem.*, 1908, (2) 77, 84; *Chem. Abs.*, 1908, 2, 2226; *Compt. rend.*, 1908, 146, 236; *Chem. Soc. Abs.*, 1908, 94 (1), 139.

[200] *Ukrainskii Khem. Zhur.*, 1930, 5, 141; *Chem. Abs.*, 1921, 25, 2690.

[201] I. G. Farbenindustrie A.-G., British Patent 381,459, 1932; *Brit. Chem. Abs.* B, 1933, 54.

[202] Fourneau and Tiffeneau, *Compt. rend.*, 1908, 146, 697.

Chapter 24

Miscellaneous Reactions of Olefins (I)

A number of industrially important addition reactions of the simple olefins, notably with sulphuric acid and halogens and halogen acids, have already been discussed in some detail.[1] In the following account some further reactions of these olefins, mostly of an additive character also, are more briefly described. Though many of these miscellaneous reactions are imperfectly understood and perhaps of only academic interest, there are indications that at least some of them may ultimately assume a position of importance in chemical industry. In one or two cases a single chemical reaction will convert olefins into chemical products which could previously be synthesized only with difficulty by a complicated series of steps from other materials. Thus, for example, olefins can be converted into higher ketones by a reaction which proceeds smoothly and gives good yields. It is more than likely that some of these less-known reactions of the lower olefins will equal, if not exceed in importance such well-known and technically important processes as the combination with sulphuric acid for the manufacture of alcohols or the reaction with hypochlorous acid in the synthesis of chlorohydrins and their related compounds. Since almost inexhaustible supplies of the lower olefins are available at very low cost, the potentialities of some of the reactions discussed in this chapter, most of which are completely unexplored from a technical standpoint, in organic chemical synthesis are great indeed.

CONDENSATION OF OLEFINS WITH AROMATIC HYDROCARBONS

The condensation of olefins with aromatic hydrocarbons in the presence of catalysts is a reaction which leads to the production of alkyl derivatives of the aromatic hydrocarbon. The importance of this reaction resides not only in the ease with which hitherto unknown or difficultly preparable alkylated aromatic hydrocarbons may be synthesized but also in the fact that certain of these alkylated hydrocarbons, particularly the polyalkylnaphthalenes, are possible synthetic lubricant hydrocarbons and their sulphonated products possess emulsifying and wetting properties. This appears to be a most fruitful field of research in organic chemistry, not only from a purely scientific standpoint but also in connection with the production of technically important organic substances. The best catalyst which has been found for bringing about this condensation is anhydrous aluminum chloride but undoubtedly other anhydrous metallic halides such as boron trifluoride, ferric chloride, or stannic chloride may be used, especially in the case of the more reactive olefins. In the presence of aluminum chloride double compounds of this chloride and hydrocarbons are frequently formed. These pasty double compounds must be decomposed with ice-water before the isolation of the desired product is attempted. Sulphuric acid will effect these condensations and catalytic addition in the vapor phase in the presence of phosphates has also been proposed. The direct combination of ethylene with benzene in the presence of aluminum chloride to produce a mixture of ethylated benzenes was studied by Balsohn[2] in 1879 and somewhat later by Gattermann, Fritz and Beck,[3] and Schleicher and Büttgenbach.[4] To effect this addition a stream of dry ethylene is passed through a suspension of aluminum chloride in dry benzene. Milligan and Reid[5] found that the reaction is considerably facilitated by high-speed stirring. This mode of ethylation, in which ethylene is not to be considered merely as a substitute for ethyl chloride, produces all the possible ethylated benzenes, including hexaethylbenzene. According to Berry and Reid,[6] the best proportion of aluminum chloride appears to be 1 mole to 13 moles of benzene and the optimum temperature is 70° C. When the stirring is stopped the reaction mixture separates sharply into two layers: a colorless top layer which contains only a trace of aluminum chloride, and a lower dark and more viscous layer in which the aluminum chloride is associated with about its own weight of hydrocarbon. It was shown that each of the hydrocarbons was partitioned between the two layers but the aluminum chloride holds the higher ethylated benzenes in preference to the lower. From mono- to tetra-ethylbenzene, the concentrations in the two layers do not differ greatly but there is a marked accumulation of pentaethylbenzene in the lower layer. Table 108 shows the proportions of the products obtained by continuously passing ethylene through 100 moles of benzene in the presence of aluminum chloride at 70° C., with efficient stirring.

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[1] See Chapters 11, 13, 14, 16, and 20.

TABLE 108.—*Products Obtained by Passing Ethylene Through Benzene in the Presence of Aluminum Chloride at 70° C.*

Ethylene Moles of	Products (Per Cent by Weight of Ethylbenzenes)						
Absorbed	C_6H_6	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-
0.20	87.9	10.9	1.24	—	—	—	—
0.56	80.5	15.2	1.67	0.71	—	—	—
1.14	31.6	35.2	21.1	4.0	2.4	2.8	2.82
1.38	37.3	30.1	11.6	6.7	3.0	3.2	8.2
1.68	35.4	23.4	13.6	6.3	4.2	3.6	13.4
3.66	0.2	1.1	10.6	56.2	11.6	1.5	18.7
5.24	—	—	—	7.0	18.8	2.4	71.8
5.74	—	—	—	—	8.5	0.9	90.6

It will be seen that continued absorption of ethylene favors the production of hexaethylbenzene. This hydrocarbon, which is a crystalline solid, is also produced in good yield by the action of ethylene under pressure at room temperature on benzene in the presence of aluminum chloride.[7]

Berry and Reid[8] also investigated the condensation of ethylene and propylene with other aromatic hydrocarbons in the presence of aluminum chloride at 70° C. Toluene was ethylated more rapidly by ethylene than benzene and the products contained a complex mixture of ethyltoluenes as well as ethylbenzenes and xylenes. Ethylation, therefore, was accompanied by splitting and rearrangement of alkyl groups. Propylene was found to combine with benzene much more slowly than ethylene under the same conditions. The reaction mixture separated into two layers, the lower being relatively larger and more difficult to decompose with water than that obtained in the ethylation of benzene. The product consisted of a mixture of isopropylated benzenes, from the higher fractions of which was isolated a crystalline solid melting at 117° C. and boiling at 260° C. at 775 mm. This compound was thought to be 1,2,4,5-tetraisopropylbenzene. Two aliphatic hydrocarbons, which boiled at 28° C. and 56° to 59° C. (diisopropyl) were also produced, probably by splitting off of alkyl groups under the influence of aluminum chloride. Table 109 shows the relative proportions of the products in the experiments of Berry and Reid on the propylation of benzene.

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[2] *Bull. soc. chim.*, 1879, (2) **31**, 539; *Chem. Soc. Abs.*, 1879, **36**, 785.
[3] *Ber.*, 1899, **32**, 1122.
[4] *J. prakt. Chem.*, 1923, **105**, 355; *Chem. Abs.*, 1923, **17**, 2873.
[5] *J.A.C.S.*, 1922, **44**, 206; *Ind. Eng. Chem.*, 1923, **15**, 1048.
[6] *J.A.C.S.*, 1927, **49**, 3142.
[7] Stanley, *J.S.C.I.*, 1930, **49**, 349T.
[8] *J.A.C.S.*, 1927, **49**, 3142.

TABLE 109.—*Products Obtained by Passing Propylene Through Benzene in the Presence of Aluminum Chloride at 70° C.*

Moles of Propylene Absorbed	Products (Per Cent by Weight of Isopropylbenzene)					
	C_6H_6	Mono-	Di-	Tri-	Tetra-	Residue
0.6	16.3	42.5	27.0	6.1	2.1	6.1
0.75	18.9	52.0	20.0	3.0	1.3	4.8
1.97	1.4	0.6	3.9	87.6	3.3	3.3
1.93	1.3	15.6	46.7	46.7	5.4	—

Examination of the diisopropylbenzene fraction showed that about 65 per cent was the meta-compound (boiling point 203.5° to 204.5° C.), whereas 1,2,4-triisopropylbenzene (boiling point 237° to 237.5° C. at 752 mm., 97° to 97.5° C. at 4 mm., D_0^0 0.8764, N_D^{25} 1.4855) constituted 75 per cent of the triisopropyl fraction.

Toluene was found to react with propylene at 70° C. in the presence of aluminum chloride much more rapidly than benzene and the products consisted of xylenes, triethylbenzenes, and m- and p-cymene, with a preponderance of p-cymene. Treatment of 276 grams of benzene with 290 grams of cyclohexene and 60 grams of aluminum chloride at 55° C. yielded 50 grams of cyclohexylbenzene, which boiled at 230° to 245° C., and a large proportion of high-boiling products.

The production of mono- and poly-alkylated aromatic hydrocarbons from aromatic hydrocarbons and olefins appears to be a general reaction in the presence of aluminum chloride. The production of tertiary-butylxylene by condensation of isobutylene with xylene in the presence of aluminum chloride has been also effected.[9] Essner and Gossin[10] obtained liquid amyltoluenes by the action of amylene on toluene in the presence of this reagent. Bodroux[11] effected the combination of cyclohexene with benzene, toluene, m-xylene, mesitylene, cymene, diphenyl, diphenylmethane, dibenzyl, naphthalene, and tetrahydronaphthalene, in the presence of aluminum chloride in carbon disulphide solution to yield cyclohexyl- and dicyclohexyl-derivatives of these hydrocarbons. From the products of the action of propylene on naphthalene in the presence of aluminum chloride at 90° C., Berry and Reid[12] isolated isopropylnaphthalene.

Cracked gasoline and kerosene fractions can be condensed with aromatic hydrocarbons in the presence of aluminum halides to yield alkylated aromatic products. The influence of the concentration of olefins (their relative proportion in the mixture), the amount of catalyst, the reaction temperature, and the method of adding the catalyst in such alkylations was studied by Tilicheyev and Kuruindin.[13] Table 110 shows the fractions which were separated from cracked paraffin and made to react with benzene, by adding them slowly to a ten-fold proportion of benzene, the olefin content of each, and the yield of products:

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[9] A.-G. für Anilin-Fabrikation, German Patent 184,230, 1906; *Chem. Zentr.*, 1907, **2**, 366.
[10] *Bull. soc. chim.*, 1885, **42**, 213; *Chem. Soc. Abs.*, 1885, **48**, 517.
[11] *Ann. chim.*, 1929, (10) **11**, 511; *Chem. Abs.*, 1929, **23**, 4936.
[12] *J.A.C.S.*, 1927, **49**, 3142.
[13] *Neft. Khoz.*, 1930, **19**, 586; *Chem. Abs.*, 1931, **25**, 3469.

TABLE 110.—*Production of Alkylated Benzenes from Cracked Paraffin Fractions.*

Cracked Paraffin Fraction	Per Cent Olefin	Yield of Alkylated Benzene
30°–40° C.	48.3	69.3% amylbenzene
Synthetic trimethylethylene		54.7% ter-amylbenzene
65°–68° C.	49.8	76% hexylbenzene
95°–98° C.	50.4	68% heptylbenzene
120°–127° C.	48.1	72% octylbenzene
145°–150° C.	52	58% nonylbenzene
168°–170° C.	49.8	62% decylbenzene
Synthetic diamylene		butyl-, amyl-, and hexyl-benzene
195°–196° C.	48.3	44% undecylbenzene
129°–139° C. at 5 mm.	28.8	48% cetylbenzene

A considerable number of processes have been developed for the production of alkylated aromatic hydrocarbons by the condensation of the lower aromatic hydrocarbons with olefins in the presence of aluminum chloride. The raw materials may be aromatic hydrocarbons such as benzene and its homologues or polynuclear hydrocarbons such as naphthalene[14] and the olefin may be one of the simple monolefins, for example, the lower gaseous unsaturated hydrocarbons. Davidson proposed to make alkylbenzenes, which can be blended with motor fuels, by condensing benzene or an alkylbenzene with olefins in the presence of aluminum or ferric chloride.[15] The reaction can be advantageously conducted with vigorous agitation, under pressure, in a countercurrent system, at a temperature near the boiling point of benzene. The production of alkylated naphthalenes by the condensation of naphthalene with gaseous olefins under pressure at a temperature above 50° C. has been suggested by Michel.[16] The products are said to be usable as lubricants for ice-machines,[16a] as insulating oils,[16b] and as motor lubricants. Michel[17] also produced alkylnaphthalenes by a similar condensation with gaseous olefins or olefin mixtures at 50° to 200° C. in the presence of aluminum chloride. For example, 128 kilograms of naphthalene and 4 kilograms of anhydrous aluminum chloride are stirred with ethylene under 20 atmospheres pressure at 100° to 200° C. The reaction is started by passing in a little dry hydrogen chloride. The ethylene is replenished until 38 kilograms have been absorbed. On distillation there are separated 25 kilograms of unchanged naph-

[14] The Edeleanu extract of kerosenes has been proposed as an appropriate aromatic material for this condensation by the I. G. Farbenindustrie A.-G., British Patent 316,274, 1929; *Brit. Chem. Abs.* **B**, 1931, 55. This patent is an addition to British Patent 299,086, 1927; *Brit. Chem. Abs.* **B**, 1928, 919.

[15] British Patent 303,505, 1928; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1929, **23**, 4568. According to Davidson (U. S. Patent 1,879,118, Sept. 27, 1932; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 401), the alkylbenzene serves to diminish spontaneous evaporation without substantially raising the end point or increasing detonation of casing-head gasoline.

[16] German Patent 550,494, 1927; addn. to German Patents 505,403, 1926; 523,691, 1926; and 525,834, 1927; *Chem. Abs.*, 1932, **26**, 4065; *ibid.*, 1930, **24**, 5766; *ibid.*, 1931, **25**, 3667; *ibid.*, 1931, **25**, 4282; all patents assigned to I. G. Farbenindustrie A.-G. See also British Patent 265,601, 1926; *Chem. Abs.*, 1928, **22**, 433; British Patent 273,665, 1927; *Brit. Chem. Abs.* **B**, 1928, 740; British Patent 295,990, 1928; *Brit. Chem. Abs.* **B**, 1930, 276; British Patent 321,187, 1928; *Brit. Chem. Abs.* **B**, 1930, 180; British Patent 323,100, 1928; *Brit. Chem. Abs.* **B**, 1930, 363. U. S. Patent 1,766,344, June 24, 1930; *Chem. Abs.*, 1930, **24**, 4051.

[16a] See Ernst and Lange, German Patent 494,429, 1925; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 2761.

[16b] See Michel, U. S. Patent 1,878,509, Sept. 20, 1932; *Chem. Abs.*, 1933, **27**, 410; British Patent 366,091, 1930; *Chem. Abs.*, 1933, **27**, 2640; both patents assigned to I. G. Farbenindustrie A.-G.

[17] U. S. Patents 1,667,214, Apr. 24, 1928; 1,741,472, Dec. 31, 1929; Re-issue 17,548, Dec. 31, 1929. See also U. S. Patent 1,878,963, Sept. 20, 1932; *Chem. Abs.*, 1933, **27**, 310; French Patent 33,807, 1927; addn. to French Patent 628,440; *Chem. Abs.*, 1929, **23**, 3718; all patents assigned to I. G. Farbenindustrie A.-G.

thalene, 110 kilograms of oil boiling at 250° to 400° C. (which consists of a mixture of β-monoethylnaphthalene, di- and poly-ethylnaphthalenes and dinaphthyl derivatives), and 25 kilograms of undistillable residue. An oil which boils between 240° C. and 340° C. is obtained by treating 132 kilograms of tetrahydronaphthalene with 2 kilograms of aluminum chloride and ethylene under pressure at 100° C.

According to Michel,[18] homologous olefins such as propylene and butylenes will react with naphthalene hydrocarbons, partially hydrogenated naphthalenes (e.g., tetrahydronaphthalene) or halogenated naphthalenes (e.g., α-chloronaphthalene or monochlorotetrahydronaphthalene) in the presence of a catalyst such as aluminum chloride, at normal or even at reduced pressures and temperatures. Under these conditions ethylene is substantially unaffected. Ethylene may then be recovered from mixtures which contain other olefins.

By passing propylene into a mixture of 128 parts of naphthalene and 4 parts of aluminum chloride at 80° C., with stirring, for example, the propylene is completely absorbed and the reaction is complete when the increase in weight amounts to 168 parts. The reaction mixture may be decomposed with water, to give propylated naphthalenes from which it is possible to separate a crystalline hydrocarbon (tetraisopropylnaphthalene melting at 125° to 126° C.) by distillation.

Treatment of 256 parts of naphthalene and 5 parts of aluminum chloride with butylene (a mixture of 1-butene and 2-butene) at 80° C. until the total increase in weight amounts to 260 parts, yields a mixture which, on distillation *in vacuo,* gives a principal fraction boiling at 200° to 250° C. at 20 mm. and consists of polybutylnaphthalenes.

Michel [19] proposed to carry out the condensation of naphthalene, or its oxygen-free derivatives, with olefins in the presence of aluminum chloride and an inert solvent such as decahydronaphthalene. Mono- and di-ethylnaphthalenes (boiling between 140° and 200° C. at 20 mm.), tetraisopropylnaphthalene, tetrabutylnaphthalene (boiling at 186° to 190° C. at 5 mm.), and other condensation products can be thus obtained.

The direct combination of olefins with aromatic hydrocarbons may be effected with catalysts other than aluminum chloride or anhydrous metallic halides. It has long been known that sulphuric acid catalyzes the direct combination of olefins with aromatic substances. Brochet [20] found that benzene and hexene reacted together in the presence of sulphuric acid to yield a hexylbenzene and other products. Kraemer and Spilker [21] showed that styrylxylenes were formed from a mixture of styrene and the xylenes in the presence of concentrated sulphuric acid.

Barbier [22] prepared tert-butyl-p-cymene by treatment of a mixture of tert-butyl alcohol and p-cymene with concentrated sulphuric acid at temperatures below 0° C. Verley [23] proposed to make alkylated aromatic hydrocarbons by shaking a mixture of an aromatic hydrocarbon, such as benzene, and an alcohol with a mixture of sulphuric acid and an alkali pyrosulphate.

Pospiech [24] obtained compounds possessing wetting and emulsifying properties by condensing aromatic sulphonic acids with olefins at 85° to 100° C. The products of this condensation are alkylated or arylalkylated aromatic sulphonic acids. For example, propylene is condensed with a mixture of α- and β-naphthalene sulphonic acids in the presence of an excess of concentrated sulphuric acid at a temperature below 100° C., or naphthalenesulphonic acid (made by sulphonating 100 kilograms of naphthalene with 150 kilograms of concentrated sulphuric acid at above 100° C.) is treated with 135 kilograms of tetrahydrobenzene and 135 kilograms of concentrated sulphuric acid at 85° to 90° C., to yield about 330 grams of a viscous condensation product. DeGroote and Keiser[24a] and DeGroote, Monson, and Wirtel[24b] used similar alkylated sulphonated aromatic compounds for breaking petroleum emulsions.

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[18] U. S. Patent 1,767,302, June 24, 1930; assigned to I. G. Farbenindustrie A.-G. Also German Patent 525,834, 1927; assigned to I. G. Farbenindustrie A.-G.

[19] U. S. Patent 1,822,358, Sept. 8, 1931; *Chem. Abs.,* 1931, **25**, 5901. See also U. S. Patent 1,741,473, Dec. 31, 1929; *Brit. Chem. Abs.* **B**, 1930, 550; British Patent 323,100, 1928; *Brit. Chem. Abs.* **B**, 1930, 363; all patents assigned to I. G. Farbenindustrie A.-G.

[20] *Compt. rend.,* 1893, 117, 115; *Chem. Soc. Abs.,* 1893, **64** (1), 635; *Bull. soc. chim.,* 1893, (3) **9**, 687.

[21] *Ber.,* 1890, **23**, 3169; *Ber.,* 1891, **24**, 2785; *cf.* Spilker and Schade, *Ber.,* 1932, **65**, 1686.

[22] *Helv. Chim. Acta,* 1932, **15**, 592; *Chem. Abs.,* 1932, **26**, 4035.

[23] German Patent 532,655, 1927; *Chem. Abs.,* 1932, **26**, 478.

[24] U. S. Patent 1,787,408, Dec. 30, 1930; *Chem. Abs.,* 1931, **25**, 713; German Patent 544,889, 1926; *Chem. Abs.,* 1932, **26**, 3519; both patents assigned to Chemische Fabrik Pott & Co.

Instead of employing free olefins for this condensation it has been suggested that substances be used which give rise to olefins under the conditions of the condensation, for example, alcohols of more than three carbon atoms, secondary- and tertiary-alkyl halides, or sulphuric acid esters of alcohols. Alkylated naphthalenesulphonic acids may be produced by condensing naphthalenesulphonic acids with isopropyl or sec.-butyl alcohols, in the presence of sulphuric acid.[25] Not only secondary and tertiary alcohols, but even primary alcohols can be dehydrated to olefins under favorable conditions. Thus, the production of n-butylnaphthalene by condensation of naphthalene with n-butanol in the presence of sulphuric acid at elevated temperatures has been described.[26]

The condensation of olefins with aromatic hydrocarbons may be carried out in the vapor or liquid phases in the presence of catalysts. For this purpose catalysts consisting of activated hydrosilicates or silica obtained therefrom have been proposed.[27] Bleaching earths, clays, or kaolins, are treated with acids, e.g., 25 per cent sulphuric acid, at 100° to 120° C. and the product is washed and dried. It is stated that polyethylnaphthalenes are formed on treating naphthalene at 250° C. with ethylene under 20 to 40 atmospheres pressure in the presence of activated bleaching earth. Similarly, cyclohexanol and benzene yield cyclohexylbenzene, and benzyl alcohol and benzene give diphenylmethane. Tetraisopropylnaphthalene[28] and other products are formed by passing propylene under pressure into a hot solution of naphthalene in decahydronaphthalene or benzine containing bleaching earth or fuller's earth as catalyst. The condensation of olefins with aromatic compounds at 300° to 400° C. at 15 to 50 atmospheres pressure in the presence of cerium metaphosphate or other phosphate, borate, or arsenate, that is, catalysts which are not reduced by hydrogen under these conditions, has also been suggested.[29] The condensation of ethylene with naphthalene, toluene, tetrahydronaphthalene, and anthracene, of propylene with toluene and of styrene with naphthalene also may be carried out.

Products which resemble lubricating oils or soft resins have been obtained by the condensation of olefins with cyclic hydrocarbons which have more than one ring in their structure.[30] This condensation may be carried out in the presence of an inert solvent, or the usual condensing agents such as aluminum chloride, zinc chloride, or activated aluminum or zinc powder. The process may be varied by allowing the condensation reactions to take place in two stages, the resins being removed at the end of the first stage. Other compounds possessing wetting properties have been prepared by condensing hydrocarbons containing three-ring nuclei (or their halogen derivatives) such as phenanthrene or anthracene with olefins in the presence of aluminum chloride and hydrogen chloride.[30a] Other catalysts and higher temperatures are used in the successive stages.

[24a] U. S. Patent 1,842,934, Jan. 26, 1932; assigned to Tretolite Co.; *Chem. Abs.*, 1932, **26**, 1763.

[24b] U. S. Patent 1,897,574, Feb. 14, 1933; assigned to Tretolite Co.; *Chem. Abs.*, 1933, **27**, 2796.

[25] I. G. Farbenindustrie A.-G., British Patent 267,132, 1926; Chemische Fabrik Pott & Co., French Patent 617,600, 1926; *Brit. Chem. Abs.* **B**, 1927, 963; Günther, U. S. Patent 1,755.179, April 22, 1930; *Chem. Abs.*, 1930, **24**, 2848; German Patent 525,158, 1925; both patents assigned to I. G. Farbenindustrie A.-G.

[26] I. G. Farbenindustrie A.-G., British Patent 319,083, 1928; *Brit. Chem. Abs.* **B**, 1929, 964; British Patent 342,399, 1929; *Brit. Chem. Abs.* **B**, 1931, 476.

[27] Rheinische Kampfer Fabrik G.m.b.H., British Patent 319,205, 1929; *Brit. Chem. Abs.* **B**, 1931, 105.

[28] I. G. Farbenindustrie A.-G., British Patent 316,951, 1928; *Chem. Abs.*, 1930, **24**, 1866; *Brit. Chem. Abs.* **B**, 1931, 194.

[29] I. G. Farbenindustrie A.-G., British Patent 327,382, 1930; *Chem. Abs.*, 1930, **24**, 5044; *Brit. Chem. Abs.* **B**, 1930, 602.

Michel[31] employed the so-called Edeleanu extract as a source of lubricating oils, by condensing it with olefins in the presence of catalysts. For example, an Edeleanu extract of viscosity 1.4° Engler at 20° C. is treated with ethylene under 20 atmospheres pressure at 140° C. in the presence of anhydrous aluminum chloride until no more ethylene is absorbed. The product is washed with water and distilled to furnish a yellow oil of viscosity 4° Engler at 20° C. and a resinous residue. According to Michel, Pungs and Galle,[32] the viscosity of mineral lubricating oils is increased by condensation with olefin gases under pressure in the presence of a catalyst, for example, by treatment with a gas containing 24 per cent of ethylene and its homologues under a pressure of 20 atmospheres at 100° C. in the presence of anhydrous aluminum chloride.

Olefins or alkyl chlorides and aromatic hydrocarbons (or alkylated aromatic hydrocarbons[32a]) can be condensed with dibasic acid anhydrides, such as phthalic, in the presence of aluminum chloride to give ketonic acids, according to Bruson.[32b] The cobalt, manganese, and lead salts of such acids (secondary amylbenzoyl-o-benzoic or p-cymoyl-o-benzoic acid, for example) are said to be driers for paints and varnishes.[32c] Similarly, olefins or low-test gasoline can be condensed with phthalic anhydride to give acids[32d] whose metallic salts can also be used as driers,[32e] or for preparing oil-soluble soaps. Salts such as those of p-secondary-butylsalicylic acid have also been suggested as siccatives for paints.[32f]

No evidence has yet been reported to demonstrate whether olefins can be condensed with completely saturated hydrocarbons, such as paraffins or cycloparaffins, to produce alkylated derivatives of these hydrocarbons.

CONDENSATION OF OLEFINS WITH PHENOLS

Just as olefins can condense with aromatic hydrocarbons to produce alkylated hydrocarbons, so alkylated derivatives of phenol can be produced also by condensation of olefins with phenols in the presence of condensing agents. Catalysts for this reaction appear to be anhydrous metallic halides, concentrated sulphuric acid, or certain activated bleaching earths.

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[30] I. G. Farbenindustrie A.-G., French Patents 665,262, 1928, and 665,402, 1928; *Chem. Abs.*, 1930, **24**, 930. Also British Patent 362,465, 1930; *Brit. Chem. Abs.* **B**, 1932, 220.

[30a] I. G. Farbenindustrie A.-G., British Patent 326,500, 1928; *Brit. Chem. Abs.* **B**, 1930, 501.

[31] German Patent 516,653, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 2845.

[32] German Patent 548,578, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 4168.

[32a] Bruson, U. S. Patent 1,934,033, Nov. 7, 1933; assigned to Resinous Products and Chemical Co.

[32b] U. S. Patent 1,889,347, Nov. 29, 1932; assigned to Resinous Products and Chemical Co.; *Chem. Abs.*, 1933, **27**, 1364.

[32c] Bruson, U. S. Patent 1,880,759, Oct. 4, 1932; assigned to Röhm and Haas Co.; *Chem. Abs.*, 1933, **27**, 1527; Resinous Products and Chemical Co., British Patent 363,394, 1930; *Chem. Abs.*, 1933, **27**, 1773; French Patent 711,198, 1930; *Chem. Abs.*, 1932, **26**, 1809.

[32d] Bruson, U. S. Patent 1,882,762, Oct. 18, 1932; assigned to Resinous Products and Chemical Co.; *Chem. Abs.*, 1933, **27**, 835; Resinous Products and Chemical Co., French Patent 711,199, 1930; *Chem. Abs.*, 1932, **26**, 1810; British Patent 356,084, 1930; *Chem. Abs.*, 1933, **27**, 1773.

[32e] Bruson, U. S. Patent 1,894,460, Jan. 17, 1933; *Chem. Abs.*, 1933, **27**, 2458; *cf.* U. S. Patent 1,933,521, Oct. 31, 1933; *Chem. Abs.*, 1934, **28**, 662; both patents assigned to Resinous Products and Chemical Co.

[32f] Bruson, U. S. Patent 1,933,520, Oct. 31, 1933; assigned to Resinous Products and Chemical Co.; *Chem. Abs.*, 1934, **28**, 662.

Sulphuric acid has been employed by a number of observers to effect the condensation of olefins with phenols. Koenigs[33] and Anschütz and Beckerhoff[34] obtained p-alkylated phenols by the action of olefins such as styrene and isoamylene on phenol in the presence of this condensing agent and Schrauth and Quasebarth[35] condensed cyclohexene with phenol under similar conditions to produce 17 per cent of p-cyclohexylphenol. It was shown by Niederl and Natelson[36] that at low temperatures, condensation of olefins such as diisobutylene with phenols (e.g., m-cresol) yield ethers, such as m-cresol diisobutyl ether. Since some of these ethers can isomerize at higher temperatures in the presence of dehydrating agents, to the corresponding p-alkylated phenol, the reaction probably proceeds as follows:

$$C_6H_5\ OH + C_nH_{2n} \longrightarrow C_6H_5\ O\ C_nH_{2n+1} \longrightarrow C_nH_{2n+1}\ C_6H_4\ OH$$

Additional evidence in support of this reaction mechanism has been advanced by Sowa, Hinton and Nieuwland,[37] who made a careful investigation of the condensation of propylene with phenol in the presence of boron trifluoride as catalyst. A whole series of isopropylated phenols and their isopropyl ethers was obtained, the quantitative relationship between the various products depending mainly upon the reaction temperature. The reactions which occurred were represented as follows: Propylene + phenol → isopropyl phenyl ether → o-isopropylphenol → o-isopropylphenyl isopropyl ether → 2,4-diisopropylphenol → 2,4-diisopropylphenyl isopropyl ether → 2,4,6-triisopropylphenol → 2,4,6-triisopropylphenyl isopropyl ether. By carrying out the reaction at 0° C., the main product obtained was isopropyl phenyl ether, which, however, was only present to a small extent when the reaction was effected at 20° C. At 40° C., the only reaction products isolated were 2,4,6-triisopropylphenol and its isopropyl ether, the latter predominating. The condensation appears to stop at this stage, for no higher products were obtained.

The condensation of cyclohexene with phenol in carbon disulphide solution under the influence of aluminum chloride was studied by Bodroux,[38] who found the main products of the reaction to consist of o- and p-cyclohexylphenols, cyclohexyl chloride, and cyclohexyl phenyl ether. The propylation of m-cresol in the presence of sulphuric acid to yield mainly thymol (together with small amounts of 1,3,5-isopropylcresol and 1,3,4-propylcresol) is described by Blagden.[39] He has also treated sulphonated phenol and o-nitrophenol with propylene and sulphonated m-cresol with ethylene.

Linner[40] suggested the condensation of olefins with phenols in the presence of aluminum chloride, ferric chloride, or zinc chloride, with a small proportion of alkyl halide or halogen acid to initiate the reaction. In the presence of a small proportion of ferric chloride, tertiary amyl chloride and phenol readily

[33] *Ber.*, 1890, **23**, 3145; *ibid.*, 1891, **24**, 3889.

[34] *Ann.*, 1903, **327**, 218; *Chem. Soc. Abs.*, 1903, **84** (1), 556; *cf.* Standard Oil Development Co., French Patent 731,556, 1932; *Chem. Abs.*, 1933, **27**, 731.

[35] *Ber.*, 1924, **57B**, 854; for the condensation of cyclohexene with phenol see also Liebermann and Hartmann, *Ber.*, 1892, **25**, 957.

[36] *J.A.C.S.*, 1931, **53**, 273; see also *ibid.*, 1931, **53**, 1928.

[37] *J.A.C.S.*, 1932, **54**, 3694.

[38] *Ann. chim.*, 1929, (10) **11**, 511; *Chem. Abs.*, 1929, **23**, 4936.

[39] British Patent 214,866, 1923; assigned to Howard & Sons, Ltd.; *Chem. Abs.*, 1924, **18**, 2715.

[40] Austrian Patent 124,281, 1931; assigned to Soc. Riechhold, Flügger and Boecking; *Chem. Abs.*, 1932, **26**, 735; French Patent 697,711, 1930; *Chem. Abs.*, 1931, **25**, 3013. U. S. Patent 1,892,990, Jan. 3, 1933; assigned to Beck, Koller and Co.; *Chem. Abs.*, 1933, **27**, 2319.

react, with the liberation of hydrogen chloride, to give para-tertiary-amylphenol.[41] Olefins absorb hydrogen chloride[42] to form the alkyl chloride. The mechanism of this Linner process can be thus inferred.

The condensation of propylene with o-, m-, or p-cresol in the presence of catalysts has also been described.[43] Catalysts include alumina, aluminum phosphate, and thorium or tungsten oxides (alone or on carriers), zinc chloride and anhydrous acids. Olefins have also been condensed with phenols in the presence of certain activated hydrosilicates.[44] The propylation of 6-chloro-m-cresol by propylene in the presence of such catalysts to yield ultimately 6-chloro-thymol has been carried out. Bleaching earth or fuller's earth has also been used to effect the condensation of olefins with phenols.[45]. Thus, propyl tolyl ether and propylated cresols are formed by passing propylene into a hot solution of m-cresol in an inert solvent containing a bleaching earth, until absorption is complete.[45a] Substituted phenols can also be produced by the condensation of phenol with ethylene under pressure at 200° to 500° C. in the presence of catalysts (such as cerium metaphosphate).[46]

The condensation of phenols with olefins in the presence of surface catalysts has been effected.[47] For example, phenol when heated with propylene under 15 to 20 atmospheres pressure at 140° C. in the presence of 10 per cent of tonsil for a short time, yielded the isopropyl ether of phenol together with a little n-propyl ether. Longer periods of heating at higher temperatures produced p-isopropylphenol and p-propylphenol. Under similar conditions. phenol and cyclohexene condensed to yield the cyclohexyl ether which then isomerized to p-cyclohexylphenol. Cresol and cyclohexene first form the ether which then rearranges to 1-methyl-4-cyclohexyl-3-hydroxybenzene. Alkylated cresol ethers are obtained by condensing olefins of more than two carbon atoms with cresol ethers in the presence of condensing agents such as aluminum chloride, sulphuric acid, or phosphoric acid.[48] The condensation of m-tolyl methyl ether with isobutylene furnishes 3-methoxy-4-tert-butyltoluene, boiling at 228° C., and with propylene, a mixture of methyl ethers of isomeric thymols, which boil at 215° to 230° C.

It appears, therefore, that the catalytic condensation of olefins with phenols is likely to prove a valuable synthetic method for the preparation of alkylated phenols and other substances.[49] These new products, commercial quantities of which have become available, are finding some application as new raw materials for the manufacture of oil-soluble synthetic resins.[50] Christiansen and Lott[50a] condensed cresol with amylene in the presence of sulphuric acid at less than 10° C. to obtain amylcresols which may be used as bactericides. The possible extension of these reactions to condensation of olefins with purely aliphatic hydroxy-compounds has also been indicated.[51] Thus, tertiary olefins can be made to react with aliphatic alcohols in the presence of sulphuric acid to yield the corresponding ethers, e.g., isobutylene can be condensed with methanol to furnish tert-butyl methyl ether. Olefins can also be condensed with unsaturated substances containing one or more carbonyl or carboxyl groups, for example, maleic acid, crotonic acid, maleic anhydride, crotonaldehyde, acrolein, and quinone.[51a] Thus, "amylene succinic acid" has been prepared by heating amylene for 2 hours at 180° C. with 20 per cent by weight of maleic anhydride. After cooling, the residue, from which unreacted amylene has been distilled, is treated with 20 per cent alkali. Two layers are formed, the upper of which consists of oily polymerization products. From the lower aqueous layer the dibasic acids formed can be precipitated with a mineral acid and purified by recrystallization from water.

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[41] Lewis, *J.C.S.*, 1903, **83**, 329. See Chapter 34.

[42] See Chapter 12.

[43] Rheinische Kampfer Fabrik G.m.b.H., British Patent 298,600, 1927; *Chem. Abs.*, 1929, **23**, 2987.

[44] Rheinische Kampfer Fabrik G.m.b.H., British Patent 319,205, 1929; *Brit. Chem. Abs.* **B**, 1931, 105.

[45] I. G. Farbenindustrie A.-G., British Patent 316,951, 1928; *Chem. Abs.*, 1930, **24**, 1866.

[45a] Hofmann and Wulff (U. S. Patent 1,898,627, Feb. 21, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2691) use boron fluoride for condensing cresol with ethylene at 300° C. to form tolyl ethyl ether.

[46] I. G. Farbenindustrie A.-G., British Patent 327,382, 1928; *Brit. Chem. Abs.* **B**, 1930, 602; *Chem. Abs.*, 1930, **24**, 5044.

[47] Schering-Kahlbaum A.-G., British Patent 308,662, 1929; *Brit. Chem. Abs.* **B**, 1930, 940.

[48] Schering-Kahlbaum A.-G., French Patent 723,377, 1931; *Chem. Abs.*, 1932, **26**, 4135; British Patent 373,896, 1931; *Brit. Chem. Abs.* **B**, 1932, 878.

[49] For the condensation of cyclohexene with the three cresols, see Boettcher, Thesis, Berlin, 1931; *Chem. Abs.*, 1931, **25**, 3662.

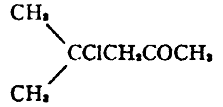
[50] For the production of such a resin from para-tertiary-amylphenol, see Hönel, French Patent 676,456, 1929; *Chem. Abs.*, 1930, **24**, 3092; Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., New York. Para-tertiary-amylphenol has been advertised to the trade as "Pentaphen" (Sharples Solvents Corp.).

[50a] U. S. Patent 1,922,153, Aug. 15, 1933; assigned to E. R. Squibb and Sons; *Chem. Abs.*, 1933, **27**, 5153.

Morrell and Egloff[51b] heated polymeric hydrocarbons such as those obtained from cracked distillates with phenolic material to 150° C. in the presence of chlorine, air, ozone, or oxides of chlorine until the mixture thickened sufficiently. The product was said to be usable for molding under pressure.

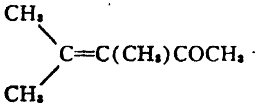
CONDENSATION OF OLEFINS WITH ORGANIC ACID CHLORIDES

The condensation of acyl chlorides with olefin hydrocarbons was observed by Kondakow,[52] who found that isobutylene reacts with acetyl chloride in the presence of zinc chloride as catalyst to produce a chloroketone of the formula



$$(CH_3)_2CClCH_2COCH_3$$

which was unstable and which, on heating, evolved hydrogen chloride with the production of mesityl oxide. In the same way, trimethylethylene reacted to produce a chloroketone which was decomposed to a methylmesityl oxide derivative. The latter reaction was also investigated by Zelinski,[53] who obtained from trimethylethylene and acetyl chloride in the presence of aluminum chloride, the unsaturated ketone



$$(CH_3)_2C{=}C(CH_3)COCH_3$$

The condensation of a cyclic hydrocarbon, C_8H_{14} (1,1,2-trimethyl-2-cyclopentene or isolaurolene), with acetyl chloride in the presence of aluminum chloride was found by Blanc[54] to furnish the corresponding unsaturated ketone. Condensation of the simple olefins, ethylene to octylene, with acetyl chloride was also investigated by Krapivin,[55] who obtained, as products, a series of unsaturated ketones of the type $CH_3.CO.CR{=}CH_2$.

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[51] Edlund and Evans, British Patent 393,753, 1933; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, 27, 5752.

[51a] Bataafsche Petroleum Maatschappij, French Patent 743,302, 1933; *Chem. Abs.*, 1933, 27, 3720.

[51b] U. S. Patent 1,744,135, Jan. 21, 1930; *Chem. Abs.*, 1930, 24, 1529; U. S. Patent 1,766,927, June 24, 1930; *Chem. Abs.*, 1930, 24, 4409; both patents assigned to Universal Oil Products Co.; *cf.* I. G. Farbenindustrie A.-G., French Patent 735,906, 1932; *Chem. Abs.*, 1933, 27, 1221.

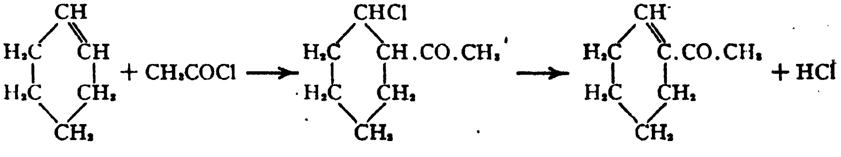
[52] *J. Russ. Phys.-Chem. Soc.*, 1894, 26, 12; *Chem. Soc. Abs.*, 1896, 70 (1), 462.

[53] *J. Russ. Phys.-Chem. Soc.*, 1899, 31, 402; see also Krapivin, *loc. cit.*

[54] *Bull. soc. chim.*, 1899, (3) 19, 699; *Chem. Soc. Abs.*, 1899, 76 (1), 630.

[55] *Bull. Soc. Imp. Nat. Moscow*, 1908, 1; *Chem. Zentr.*, 1910, 1, 1335; *Chem. Abs.*, 1911, 5, 1281.

A very careful investigation of this reaction in the case of cyclohexene and acetyl chloride was made by Darzens.[56] From the reaction of 82 grams of cyclohexene with 78 grams of acetyl chloride in the presence of 138 grams of aluminum chloride in 600 grams of carbon disulphide in the cold, was obtained a chloroketone which was readily decomposed into cyclohexenyl methyl ketone by a weak base. The yield of this unsaturated ketone was 50 grams or about 42 per cent of the theoretical. The reaction mechanism proposed by Darzens is represented by the following scheme:



In order to recover the reaction product it was necessary to decompose the aluminum chloride complex with ice-water. Darzens tested the efficacy of various other anhydrous metallic halides in promoting this reaction. The chlorides of sulphur, copper, mercury, and stannous chloride were inactive; the trichlorides of boron, iron, and antimony catalyzed the reaction but with lower yields than those with aluminum chloride, and titanium tetrachloride was satisfactory. However, stannic chloride was found to give even better results than aluminum chloride. Thus, treatment of 82 grams of cyclohexene and 78.5 grams of acetyl chloride in 600 grams of carbon disulphide with 250 grams of stannic chloride produced ultimately 60 grams of cyclohexenyl methyl ketone, which corresponded to a yield of 50 per cent.

The condensation of ethylene with benzoyl chloride in the presence of aluminum chloride in carbon disulphide solution was investigated by Norris and Couch[57] and found to yield phenyl vinyl ketone as follows, though the yield was poor:

$$C_2H_4 + C_6H_5COCl \longrightarrow CH_2{=}CHCOC_6H_5 + HCl$$

Wieland and Bettag[58] examined similar reactions, namely, the condensation of cyclohexene and trimethylethylene with acetyl and benzoyl chlorides in carbon disulphide solution in the presence of aluminum chloride at low temperatures. In this way the unstable β-chloroketones were isolated in the form of their semicarbazones. It was also shown that, on warming in carbon disulphide solution with aluminum chloride, these intermediate chloroketones are readily converted into vinyl ketones with elimination of hydrogen chloride. For this reason, unless a low temperature is maintained during the condensation of olefins with acyl chlorides, the unstable intermediate chloroketones are converted into the unsaturated ketones. Wieland and Bettag explained the reaction on the assumption of the formation of an aluminum chloride-acid chloride complex. Treatment of 20 grams of cyclohexene, and 30 grams of acetyl chloride in 75 grams of carbon disulphide with 35 grams of anhydrous aluminum chloride at low temperatures yielded 15.8 grams of chlorocyclohexyl methyl ketone which, in turn, readily lost hydrogen chloride to form tetrahydroacetophenone (cyclohexenyl methyl ketone). Similarly, benzoyl chloride and cyclohexene yielded 2-chlorocyclohexyl phenyl ketone which was converted into tetrahydrobenzophenone:

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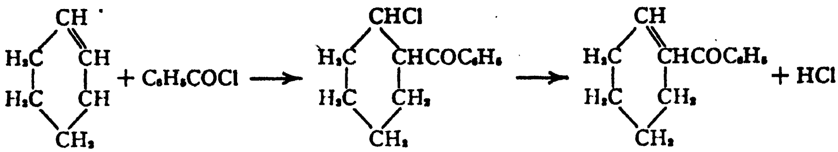
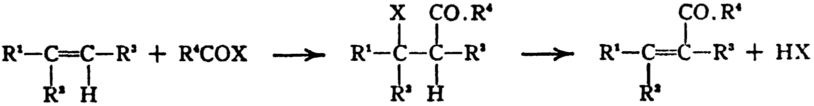
[56] *Compt. rend.*, 1910, 150, 707; *Chem. Abs.*, 1910, 4, 2093.
[57] *J.A.C.S.*, 1920, 42, 2329.
[58] *Ber.*, 1922, 55, 2246.



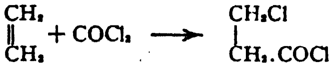
It is evident from the foregoing results that the condensation of olefins with acid chlorides is a very general reaction leading to the formation of an unstable β-chloroketone which loses hydrogen chloride to yield an alkyl vinyl ketone. This general reaction may be written:



$$R^1{-}\underset{R^2}{C}{=}\underset{H}{C}{-}R^3 + R^4COX \longrightarrow R^1{-}\overset{X}{\underset{R^2}{C}}{-}\overset{CO.R^4}{\underset{H}{C}}{-}R^3 \longrightarrow R^1{-}\underset{R^2}{C}{=}\overset{CO.R^4}{C}{-}R^3 + HX$$

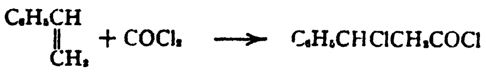
where R^1, R^2, R^3, and R^4 are alkyl or aryl groups and X is a halogen atom. The condensation can apparently be effected by aluminum chloride, stannic chloride or titanium tetrachloride. Since aluminum chloride tends to polymerize olefins, for condensing the more reactive olefins with acid chlorides the milder catalysts such as stannic chloride can be employed with advantage. As the higher olefins are much more stable it would appear quite feasible to use aluminum chloride in condensing these substances with acid chlorides to produce higher ketones. The above reaction is worthy of further study not only on account of its obvious technical significance in the synthesis of higher ketones, but also because of its undoubted scientific interest.

The condensation of ethylene with acyl chlorides in the presence of a Friedel-Crafts condensing agent has been employed to produce substituted vinyl ketones.[59] A special case of this reaction is the condensation of phosgene with unsaturated hydrocarbons to yield chloro-acid chlorides. The reaction of phosgene with ethylene under the influence of light to yield β-chloropropionyl chloride according to the scheme,



$$\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix} + COCl_2 \longrightarrow \begin{matrix}CH_2Cl\\ | \\ CH_2.COCl\end{matrix}$$

was observed by Lippmann,[60] and later Pace[61] showed that this reaction can take place under the influence of aluminum chloride. The reaction is carried out by passing phosgene into a solution of the olefin in toluene at 35° to 40° C. in the presence of aluminum chloride until no more is absorbed. Under these conditions, ethylene yields β-chloropropionyl chloride, which boils at 144.5° C.; and isoamylene, β-chloro-γ-methylvaleryl chloride, which boils at 168° C. Styrene and phosgene react to yield β-chloro-β-phenylpropionyl chloride (which melts at 139° C. with decomposition). This latter reaction may be represented thus:



$$\begin{matrix}C_6H_5CH\\ \| \\ CH_2\end{matrix} + COCl_2 \longrightarrow C_6H_5CHClCH_2COCl$$

This synthesis of β-chloroacid chlorides appears to be of interest because of its possible large-scale use in the production of acids similar to acrylic acid and its homologues, since β-chloro acids readily lose hydrogen chloride to form unsaturated acids of that type. For example, esters of acrylic acid are said to be produced by heating esters of β-chloropropionic acid in the presence of catalysts such as barium phosphate, concentrated sulphuric or phosphoric acid, or zinc chloride.[62]

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[59] Schoeller and Züllner, U. S. Patent 1,737,203, Nov. 26, 1929; assigned to Schering-Kahlbaum A.-G.

[60] *Ann.*, 1864, 129, 81.

[61] *Gazzetta*, 1929, 59, 578; *Brit. Chem. Abs.* A, 1929, 1419.

CONDENSATION OF OLEFINS WITH BASES

The combination of ammonia and amines with olefins is a typical example of reaction which, although extremely promising from a scientific and technical standpoint, has received practically no attention from those interested in the chemical utilization of the olefins. On the purely scientific side, Taylor and Emeléus[63] studied the photochemical reaction of ethylene with ammonia and although the production of organic basic products was noted, the exact chemical nature of these products was not determined. Evidence from other sources, however, leads to the conclusion that the catalytic combination of olefins with ammonia results primarily in the formation of an alkylamine, thus:

$$C_2H_4 + NH_3 \longrightarrow C_2H_5.NH_2$$

and this reaction is in all probability reversible within certain temperature limits. At higher temperatures, secondary changes may occur with the production of nitriles and cyclic bases.

The direct catalytic combination of ethylene and ammonia in the vapor phase at elevated temperatures and increased pressures is stated by Wietzel[64] to produce ethylamine. The product obtained by reducing ammonium molybdate in a current of hydrogen, can be used as a catalyst for this process. The direct combination of ethylene and primary or secondary amines at temperatures up to 400° C., in the presence of a catalyst to furnish secondary and tertiary organic bases, has also been suggested by Nicodemus and Schmidt.[65] Activated hydrosilicates may be used as catalysts for the alkylation of ammonia and amines by ethylene under pressure.[66] The condensation of aniline with ethylene to produce substituted anilines, as well as tertiary bases containing heterocyclically combined nitrogen, has also been stated to take place in the presence of cerium metaphosphate (or other phosphate, borate, or arsenate not reducible with hydrogen) at 200° to 400° C. under pressures above atmospheric.[67]

Alkaline earth cyanamides have been prepared by passing ammonia and olefins over oxides or carbonates of the alkaline earths at 400° to 1000° C.[67a]

The condensation of ethylene with ammonia with the production of acetonitrile has been effected, for example,[68] by passing a mixture of 10 volumes of ammonia, 10 volumes of ethylene, 30 volumes of hydrogen, and 5 volumes of nitrogen over zinc sulphate on silica gel at 450° C. A 95 per cent yield of acetonitrile is thus obtained. The formation of acetonitrile can be explained on the assumption that ethylamine, which is first formed, undergoes thermal dehydrogenation to acetonitrile:

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[62] I. G. Farbenindustrie A.-G., British Patent 351,518, 1930; *Brit. Chem. Abs.* B, 1931, 1003.

[63] *J.A.C.S.*, 1931, 53, 562. See also *ibid.*, 1931, 53, 3370.

[64] German Patent 479,079, 1925; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 305.

[65] German Patent 479,351, 1927; *Chem. Abs.*, 1929, 23, 4709; German Patent 516,765, 1928; *Chem. Abs.*, 1931, 25, 1839; both patents assigned to I. G. Farbenindustrie A.-G. See also British Patent 283,163, 1927; *Chem. Abs.*, 1928, 22, 3892.

[66] Rheinische Kampfer Fabrik G.m.b.H., British Patent 319,205, 1929; *Brit. Chem. Abs.* B, 1931, 105.

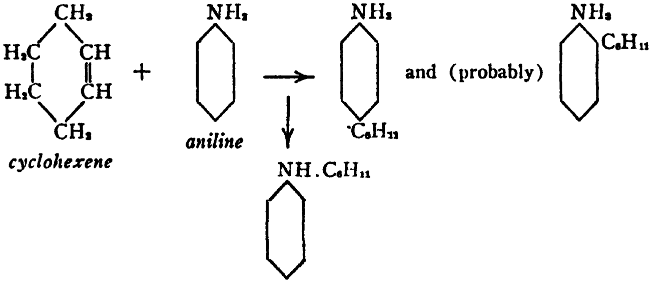
[67] I. G. Farbenindustrie A.-G., British Patent 327,382, 1928; *Chem. Abs.*, 1930, 24, 5044.

[67a] I. G. Farbenindustrie A.-G., British Patent 368,424, 1930; *Chem. Abs.*, 1933, 27, 2255.

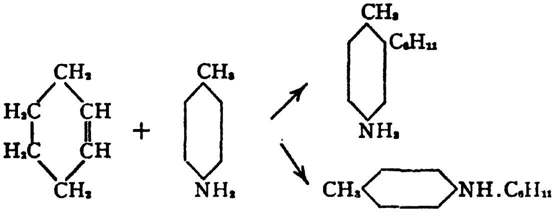
[68] I. G. Farbenindustrie A.-G., British Patent 283,163, 1928; *Brit. Chem. Abs.* B, 1929, 275; French Patent 38,072, addn. to French Patent 656,614.

$$C_2H_4 + NH_3 \longrightarrow CH_3CH_2NH_2 \longrightarrow CH_3CN + 2H_2$$

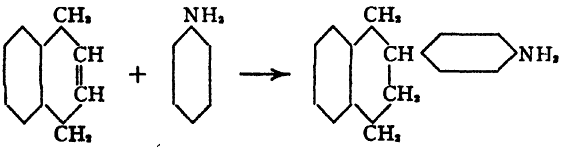
Olefinic hydrocarbons can be condensed with aniline or similar arylamines by heating the reactants together in sealed tubes to temperatures up to 270° C. Hickinbottom[69] found that trimethylethylene reacted with aniline cobaltochloride, cobaltobromide, or hydrobromide, to yield the corresponding salts of p-amino-tert-butylbenzene. Later[70] he observed that cyclohexene condensed with aniline and its hydrochloride, when heated in sealed tubes at 200° to 270° C., to produce 4-aminophenylcyclohexane together with an isomeric primary base, probably 2-aminophenylcyclohexane, and also some cyclohexylaniline. The reaction can therefore be represented as follows:



In a similar way, cyclohexene and p-toluidine yielded a mixture from which 4-amino-3-cyclohexyltoluene and cyclohexyl-p-toluidine were isolated.



The condensation of 1,4-dihydronaphthalene with a mixture of aniline and its hydrochloride by heating in a sealed tube at 200° to 300° C. yielded mainly 2-p-aminophenyl-1,2,3,4-tetrahydronaphthalene, as represented:



It is evident, therefore, that two main types of condensation occur in the condensation of olefins with primary arylamines under the conditions studied by

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[69] *J.C.S.*, 1932, 2396.

[70] Hickinbottom, *J.C.S.*, 1932, 2646.

Hickinbottom, namely (1) a direct alkylation of the aromatic nucleus with the production of an alkylated primary arylamine, and (2) alkylation of the amino-group with the formation of a secondary base.

Resinous condensation products of carbazole (or its derivatives) with olefins have also been described.[71] Mono- or poly-alkylated carbazoles or higher condensation products are said to be obtained by heating carbazoles with olefins at 100° to 200° C. in the presence of aluminum chloride, fuller's earth, tonsil, or frankonite,* in an inert solvent such as light petroleum. Propylene condenses with carbazole to give a soft resin, which boils at 210° to 240° C. at 1 mm. and which is probably diisopropylcarbazole, and with N-ethylcarbazole also to form a soft resin which boils at 200° to 230° C. at 1 mm. Cyclohexene and carbazole yield a hard resin which distils at 270° to 340° C. at 1 mm.

[71] Michel, U. S. Patent 1,916,629, July 4, 1933; *Chem. Abs.*, 1933, **27**, 4700; British Patent 327,746, 1928; *Brit. Chem. Abs.* **B**, 1930, 625; both patents assigned to I. G. Farbenindustrie A.-G.

Chapter 25

Miscellaneous Reactions of Olefins (II)

In the preceding chapter were discussed some of the miscellaneous reactions of the simpler olefins with the more generally known types of organic compounds, such as aromatic hydrocarbons and phenols. In this chapter are included reactions with a number of other substances such as sulphur dioxide, ketones, and nitrogen trichloride. The action of sulphonating agents on olefins to yield derivatives of ethionic acid is discussed in Chapter 46. With the exception of those reactions involving the use of oxides of nitrogen, which have been employed for the oxidation of petroleum hydrocarbons (see Chapter 39), these reactions apparently have been applied industrially to only a limited extent. Some of them, however, are the basis for analytical procedures, e.g., the estimation of unsaturated hydrocarbons with iodine monochloride (particularly for edible oils and fats), or with sulphur monochloride or mercuric acetate (for the lighter petroleum distillates). These reactions are of some interest both from the standpoint of the general properties and possible derivatives of the simpler olefins obtained from petroleum hydrocarbons, especially those from cracking operations.

CONDENSATION OF OLEFINS WITH KETONES

Little work has been reported of the direct combination of olefins with ketones. Brown,[1] however, synthesized higher ketones, for example, methyl propyl ketone, by condensation of an olefin (ethylene) with a ketone (acetone). Pressures of over 50 atmospheres and a catalyst—a mixture of zinc and chromium oxides and zinc chloride—which accelerates hydrogenation and dehydrogenation are recommended. If this reaction should prove to be a general one for the alkylation of ketones, it would present an interesting aspect. Presumably ethylene and acetone react in the following manner:

$$C_2H_4 + CH_3COCH_3 \longrightarrow C_3H_7COCH_3$$

REACTION OF SULPHUR DIOXIDE AND SULPHITES WITH OLEFINS

Sulphur dioxide, sulphurous acid, or sulphites combine directly with many olefins under appropriate conditions.[2] The products, unlike those obtained by the action of sulphuric acid on the monolefins, are not esters of the corresponding alcohols, but are very frequently stable sulphonic acids or condensed sulphur compounds of the sulphone type. In both of these types of compounds, the sulphur atom is linked directly to a carbon atom and hydrolysis to an alcohol is impossible. The reaction with sulphurous acid is greatly influenced by the introduction of a carbonyl group in a position adjacent to the double bond, as in the α-unsaturated ketones. This discussion, however, is limited to the reactions of the simple monolefin hydrocarbons.

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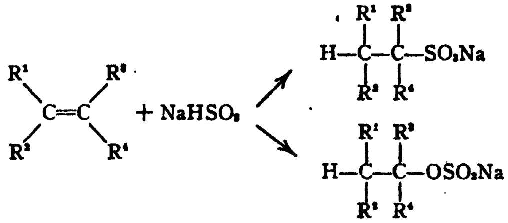
[1] U. S. Patent 1,757,830, May 6, 1930; assigned to Commercial Solvents Corp.; *Chem. Abs.*, 1930, 24, 3247.

[2] The addition of sulphites to acrylic, crotonic, cinnamic and other unsaturated acids was studied by Hägglund and Ringbom (*Z. anorg. allgem. Chem.*, 1926, 150, 231; *Chem. Abs.*, 1926, 20, 1165).

Matthews and Elder[3] stated that sulphur dioxide can combine with butylene and the amylenes under the influence of heat and light with the production of amorphous horn-like solids, that from butylene having the composition $(C_4H_8SO_2)_n$. The direct combination of ethylene hydrocarbons with sodium, potassium, or ammonium bisulphite was studied by Kolker and Lapworth.[4] The main products of the reaction were the salts of alkylsulphonic acids, admixed with variable proportions of other salts, possibly alkyl bisulphites. Kolker and Lapworth expressed this result by the general reaction:

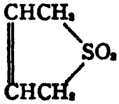


Cyclohexene was shaken with 0.25 molar ammonium bisulphite solution and kieselguhr at ordinary temperature for several days. Kieselguhr, used as an emulsifying agent, was found to have a favorable influence on the yield of sulphonate, especially when excess bisulphite was used. The product was cyclohexanesulphonic acid, isolated as its soluble barium salt. Ethylene and 0.25 molar ammonium bisulphite solution at ordinary temperature and pressure yield ethanesulphonic acid (amide, m.p. 59° to 60° C., soluble in water) and technical amylene yielded 86 per cent of crude soluble barium salts consisting of true sulphonic acid derivatives. From dipentene there was obtained mainly barium menthanedisulphonate.

Seyer and King[4a] found that pure cyclohexene did not react with dry sulphur dioxide. The presence of oxygen, however, caused the formation of an insoluble compound, $(C_6H_{10}SO_2)_x$. Cyclohexadiene, on the other hand, reacted readily even in the absence of oxygen to form a white amorphous compound, $(C_6H_8SO_2)_x$.

The direct combination of styrene with bisulphites was investigated by a number of workers[5] but with somewhat inconclusive results.

Sulphur dioxide reacts with diolefins[6] to form polymerized sulphones, of the type $(C_nH_{2n-2}SO_2)_n$. It has been stated, however, that in the presence of stabilizing substances, particularly polyhydric phenols, unpolymerized sulphones can be obtained.[7]. For example, butadiene, liquid sulphur dioxide, and 1 per cent of quinol react slowly at 15° C. to yield the sulphone



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[3] British Patent 11,635, 1914; *J.S.C.I.*, 1915, 34, 670.

[4] *J.C.S.*, 1925, 127, 307.

[4a] *J.A.C.S.*, 1933, 55, 3140.

[5] von Miller, *Ann.*, 1877, 189, 340. Labbé, *Bull. soc. chim.*, 1899, (3) 21, 1077; *Chem. Soc. Abs.*, 1900, 78 (1), 149. DuPont and Labaune, *Sci. Ind. Bull.*, 1912, (3) 7, 3; *Eighth Inter. Congr. Applied Chem.*, 1912, 25, 357; *Chem. Abs.*, 1913, 7, 2188.

[6] deBruin, *Verslag Akad. Wetens.*, 1914, 23, 445; *Chem. Abs.*, 1915, 9, 623. Staudinger, German Patent 506,839, 1929; *Chem. Abs.*, 1931, 25, 522.

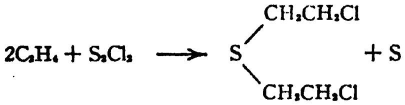
[7] Staudinger, British Patent 361,341, 1930: *Brit. Chem. Abs.* B, 1932, 301.

Corresponding products may be obtained from substituted butadienes and from isoprene. All such products are decomposed by heating to 120° C.

On treating unsaturated fatty acids or esters (e.g., train oil) with air and a sulphite or bisulphite a mixture containing partly oxidized and partly sulphited products which form emulsions with hot water results. Such emulsions can be used for the treatment of leather.[7a]

REACTIONS OF SULPHUR AND SELENIUM CHLORIDES WITH OLEFINS

The reaction of sulphur chloride and ethylene was first investigated by Despretz,[8] the product being an unpleasant-smelling viscous liquid. Guthrie [8a] later described a product made in a similar manner, which was isolated without distillation and which had the empirical formula $C_4H_8Cl_2S_2$. Pope [9] subsequently showed that this was merely a solution of sulphur in ββ′-dichlorodiethyl sulphide and that the reaction proceeded in the following manner:



$$2C_2H_4 + S_2Cl_2 \longrightarrow S\begin{cases} CH_2CH_2Cl \\ CH_2CH_2Cl \end{cases} + S$$

It was found that the reaction must be carried out at temperatures below 70° C. to prevent considerable decomposition which otherwise ensues. The further remarkable fact was demonstrated, namely, that almost quantitative yields of ββ′-dichlorodiethyl sulphide are obtained by using ethylene containing a trace of alcohol vapor, whereas pure ethylene does not yield so pure a product.

ββ′-Dichlorodiethyl sulphide was used extensively during the World War as a poison gas (mustard gas or yperite) and was the most toxic of all such gases then available. As far as is known it is not employed in chemical synthesis, though it offers distinct possibilities in that direction.[10] Dichloroethyl sulphide may be used in the preparation of paints for the protection of ship bodies from deposits of shells.[10a]

The reaction of sulphur chloride with other olefins has been little investigated, but polymerization appears to be the main result. When propylene is treated with sulphur chloride at 50° to 60° C., condensation to dark colored semi-solid materials occurs.[11]

Mineral oils which had been subjected to the influence of light in the presence of aluminum sulphate can be converted to a rubber substitute, according to Girón,[11a] by heating with sulphur or sulphur chloride and magnesium oxide.

[7a] I. G. Farbenindustrie A.-G., British Patent 387,693, 1931; *Brit. Chem. Abs.* B. 1933, 341.

[8] *Ann. chim. phys.*, 1822, (2) **21**, 428; see Schotz, "Synthetic Organic Compounds," D. Van Nostrand Co., New York, 1925, 296.

[8a] *J.C.S.*, 1860, **12**, 116; *ibid.*, 1861, **13**, 134; *Ann.*, 1861, **119**, 91; *ibid.*, 1862, **121**, 106; see also Nieumann, *Ann.*, 1860, **116**, 288. Other methods of preparing this compound were given by Meyer (*Ber.*, 1886, **19**, 3260) and by Clarke (*J.C.S.*, 1912, **101**, 1583).

[9] Pope, *J.S.C.I.*, 1919, **38**, 344R; Gibson and Pope, *J.C.S.*, 1920, **117**, 271; Pope, *J.C.S.*, 1921, **119**, 634.

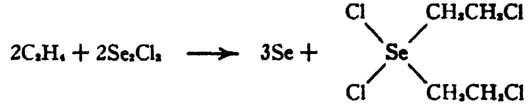
[10] For some of the reactions and derivatives of this compound see Helfrich and Reid, *J.A.C.S.*, 1920, **42**, 1208. The description of a plant for the manufacture of mustard gas is given by Quinan, *Ind. Chem.*, 1931, **7**, 474, 491; *Brit. Chem. Abs.* B, 1932, 330. For a review of the preparation, chemical and physiological properties of mustard gas and the treatment of gas cases, see Melckebeke, *J. pharm. Belg.*, 1932, **14**, 93; *Chem. Abs.*, 1932, **26**, 3230.

[10a] Varshavskii and Yakubovich, Russian Patent 28,267, 1932; *Chem. Abs.*, 1933, **27**, 3835.

[11] Coffey, *J.C.S.*, 1921, **119**, 94. *Cf.* Conant, Hartshorn and Richardson, *J.A.C.S.*, 1920, **42**, 585.

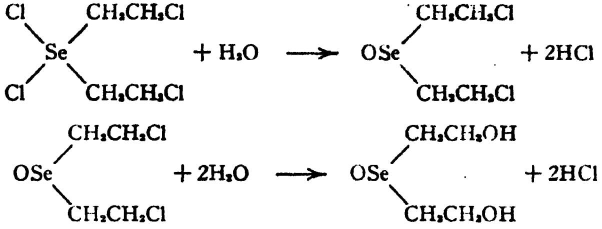
[11a] French Patents 714,953 and 714,954, 1931; *Chem. Abs.*, 1932, **26**, 1768.

Ethylene reacts with *selenium monochloride*[12] to yield free selenium and ββ'-dichlorodiethyl selenide dichloride, thus:



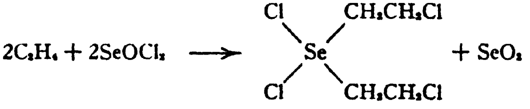
It was shown by Boord and Cope[13] that this reaction actually takes place in two stages, the free selenide being produced in the presence of an excess of ethylene while the selenide dichloride is always formed when the selenium monochloride is in excess. Similar reactions were observed in the case of propylene and butylene.

Hydrolysis of these selenide dichlorides results in the elimination of the chlorine.[14] In this manner ββ'-dichlorodiethyl selenide dichloride is converted to ββ'-dichlorodiethyl selenide oxide and this in turn to ββ'-dihydroxydiethyl selenide oxide.



Heating ββ'-dichlorodiethyl selenide dichloride to 120° to 130° C. gives selenium and ethylene chloride.

The reaction between *selenium oxychloride* and several of the monolefins has been studied by Frick.[15] It was found that the corresponding chloroalkyl selenide dichlorides are always produced regardless of whether the olefin or the oxychloride is in excess. Since selenium dioxide is the only other product of the reaction, the change can be represented, in the typical case of ethylene, by



or, generally

$$2C_nH_{2n} + 2SeOCl_2 \longrightarrow (ClC_nH_{2n})_2SeCl_2 + SeO_2$$

Thus, on passing dry ethylene into a solution of selenium oxychloride in anhydrous chloroform, ββ'-dichlorodiethyl selenide dichloride was obtained as white crystals, which melted at 121.5° C. In the same way propylene, butene-2 and amylene yielded the corresponding propyl, butyl, and amyl derivatives, respectively.

Lenher[16] recommended selenium oxychloride as a solvent for the removal of unsaturated hydrocarbons from mixtures with saturated hydrocarbons, as the latter do not dissolve in this solvent.

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[12] Bausor, Gibson and Pope, *J.C.S.*, 1920, 117, 1453; Heath and Semon, *Ind. Eng. Chem.*, 1920, 12, 1101.

[13] *J.A.C.S.*, 1922, 44, 395.

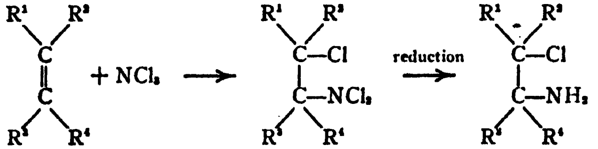
[14] Smedslund, *Finska Kem. Medd.*, 1932, 41, 13; *Brit. Chem. Abs.* A, 1933, 374.

[15] *J.A.C.S.*, 1923, 45, 1795.

[16] U. S. Patent 1,473,350, Nov. 6, 1923; *Chem. Abs.*, 1924, 18, 401.

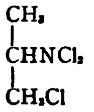
Reactions of Nitrogen Trichloride and Nitrosyl Chloride with Olefins

Nitrogen trichloride combines directly with many olefins in dry carbon tetrachloride solution at low temperatures (—10° C.) with the formation of C-chloro-N-dichloramines, many of which readily undergo reduction in the presence of dry hydrogen chloride to yield monochloro-derivatives of aliphatic amines. These reactions may be represented in the following general manner:



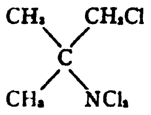
They have been investigated by Coleman and his collaborators.[17] Great differences were found in the rate of reaction of the individual simple olefins with this reagent. This difference is indicated by the fact that at 20° to 25° C., two weeks or more are required for the completion of the reaction with ethylene, while with isobutylene the reaction, even at —45° to —50° C., is complete within two or three hours.

Ethylene reacts with nitrogen trichloride to form nitrogen, ammonium chloride, ethylene dichloride, and 2-chloro-1-dichloramino-ethane, the latter compound being converted by hydrogen chloride into 1-amino-2-chlorethane. Propylene reacts more rapidly than ethylene to yield similar products, but only one of the two possible chloramines is formed:



$$\begin{array}{l} CH_3 \\ | \\ CHNCl_2 \\ | \\ CH_2Cl \end{array}$$

With isobutylene, a stable chloramine of the constitution



was formed. This compound was not reduced by hydrochloric acid (as were its homologues) but was converted into its hydrochloride. Butene-2 combines with nitrogen trichloride fairly rapidly with the formation of a moderate yield of 2-chloro-3-dichloraminobutane, readily convertible into 2-chloro-3-aminobutane. Butene-1 yields only one of the two possible isomers, namely, 1-chloro-2-dichloraminobutane. Trimethylethylene yielded no chloramine but only chlorinated derivatives. Stable compounds were obtained from pentene-2 and cyclohexene.

The behavior of certain aryl-substituted olefins toward nitrogen chloride was also investigated. Styrene and stilbene react fairly rapidly with nitrogen trichloride in carbon tetrachloride solution to form nitrogen, the dichloride of the hydrocarbon, a small amount of ammonium chloride and a C-chloro-N-dichloramine, which in each case is readily convertible to the corresponding C-chloramine. The constitution of the bases formed are as follows:

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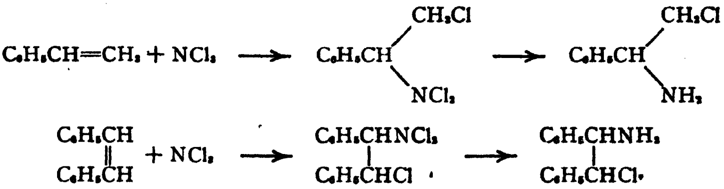
[17] Coleman and Howells, *J.A.C.S.*, 1923, 45, 3084; Coleman, Mullins and Pickering, *J.A.C.S.*, 1928, 50, 2739; Coleman and Campbell, *J.A.C.S.*, 1928, 50, 2754.

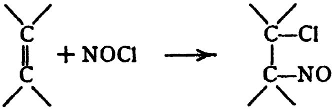


Several other aromatic olefins were studied, namely, 1,1-diphenylethylene, 1,1-diphenylpropene-1, triphenylethylene, and tetraphenylethylene. None of these yielded stable addition products with nitrogen trichloride.

The reaction of *nitrosyl chloride* with unsaturated hydrocarbons was first observed with the terpene hydrocarbons by Tilden and Shenstone.[18] It soon proved a valuable reagent for the study of these complex substances, with which it frequently forms characteristic crystalline addition compounds useful for identification purposes.[19] The first observation of the addition of nitrosyl chloride to simple olefins appears to have been made with amylene.[20]

Of the olefins which are capable of combining additively with nitrosyl chloride, the following types may be mentioned: trimethyl- and tetra-methylethylenes,[21] cyclohexenes,[22] ethylene derivatives of the type $R_2C{=}CH_2$, and hydrocarbons,[23] having a semicyclic double bond and a side chain, such as methylenecyclopentane. As a general rule, unsaturated hydrocarbons possessing the structure $>C{=}CH_2$ or $—CH{=}CH_2$ do not normally yield crystalline products with nitrosyl chloride. On the other hand those with the structure $R_2C{=}CR_2$ usually form crystalline nitrosochlorides.[24]

The action of nitrosyl chloride on olefins to give nitrosochlorides may be represented by



These nitrosochlorides, which are conveniently prepared by the addition of concentrated hydrochloric acid to a solution of the olefin and ethyl nitrite in glacial acetic acid at 10° C., are generally crystalline, bimolecular solids.[25] On treatment with alkalies they readily yield oximes, from which ketones may be obtained, so that they are often valuable in deciding questions of constitution. For example, on carefully warming the nitrosochloride of trimethylethylene with alkalies the isomeric oxime is obtained.

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[18] *J.C.S.*, 1877, 1, 554.

[19] Wallach, *Ann.*, 1888, 245, 246; *Chem. Soc. Abs.*, 1888, 54, 1098; *Ann.*, 1889, 252, 106; *Chem. Soc. Abs.*, 1889, 59, 1069; Wallach and Otto, *Ann.*, 1889, 253, 249; *Chem. Soc. Abs.*, 1890, 58, 169.

[20] Tonnies, *Ber.*, 1879, 12, 169.

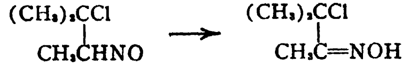
[21] Schmidt, *Ber.*, 1902, 35, 2323, 3727. Thiele, *Ber.*, 1894, 27, 454.

[22] Baeyer, *Ann.*, 1894, 278, 108. Wallach, *Ann.*, 1905, 343, 40.

[23] Wallach, *Ann.*, 1906, 347, 316.

[24] Wallach, *Ann.*, 1887, 241, 312. Schmidt and Austin, *Ber.*, 1903, 36, 1768. Thiele, *Ber.*, 1894, 27, 455.

[25] Baeyer, *Ber.*, 1895, 28, 639. Wallach, *Ber.*, 1895, 28, 1308.



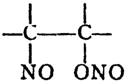
$$\begin{array}{c}(CH_3)_2CCl\\ |\\ CH_3CHNO\end{array} \longrightarrow \begin{array}{c}(CH_3)_2CCl\\ |\\ CH_3C{=}NOH\end{array}$$

Nitrosochlorides may be condensed with amines to yield stable condensation products.

Among the simple olefins, the ability to combine directly with nitrosyl chloride increases with increasing molecular weight and particularly with the introduction of methyl groups into the molecule. While propylene combines with nitrosyl chloride to form both propylene dichloride and propylene nitrosochloride, ethylene forms only ethylene dichloride.[26]

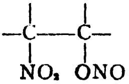
Reaction of Nitrogen Oxides with Olefin Hydrocarbons

When nitrous acid fumes are allowed to react with olefins at low temperatures a number of products are obtained, among which the so-called nitrosites and nitrosates are of importance. These substances, which in the solid state are usually bimolecular and hence are called bisnitrosites and bisnitrosates, are characterized by the following groupings:



$$-\underset{\mathrm{NO}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\underset{\mathrm{ONO}}{\underset{|}{\overset{|}{\mathrm{C}}}}-$$

nitrosites



$$-\underset{\mathrm{NO_2}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\underset{\mathrm{ONO}}{\underset{|}{\overset{|}{\mathrm{C}}}}-$$

nitrosates

The action of pure nitrogen tetroxide (N_2O_4) on olefins gives rise to solid bisnitrosates[27] but the yields are very poor, being often only about 10 per cent of those obtained with amyl nitrite and nitric acid at —10° C.[28] The formation of solid compounds with nitrogen peroxide appears to be a general property of olefins which contain the double bond between a secondary and a tertiary or between two tertiary carbon atoms. The experiments of Schaarschmidt and Hofmeier showed that the addition of nitrogen peroxide to various olefins is accompanied by oxidation and that the addition compounds undergo internal oxidation, particularly if the temperature of the reaction is allowed to rise, resulting in the reduction of nitric oxide residues mainly to nitrogen. It seems probable that the phases of the addition may correspond with the production of the forms

$—CH(NO)CHONO_2—$
$—CH(NO_2)CHONO—$
$—CH(NO_2)CHNO_2—$
and $—CH(ONO)CH(ONO)—$

The bisnitrosates react readily with aniline to give uniform yields (70-80 per cent) of the corresponding nitrolamines. Thus, 2-methylpentene-2 nitrosate condenses with aniline to yield 2-methylpentene-2 nitrolaniline, a solid melting at 86° C.

Demyanov and Williams[29] made addition compounds of nitrogen trioxide and tetroxide with unsaturated hydrocarbons. Some of these were crystalline and stable, while others were liquids and sometimes decomposed violently. They also reported that: (1) reduction of the addition products of nitrogen oxides to unsaturated hydrocarbons may serve for the preparation of diamines or hydroxyamines; and (2) no direct nitration of an unsaturated fatty nitro-compound by nitric acid is known to occur, therefore nitro-compounds formed are decomposition products of the original addition compounds.

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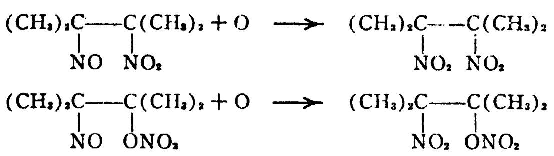
[26] Tilden and Sudborough, *J.C.S.*, 1893, 63, 479. *Cf.* Tilden and Forster, *J.C.S.*, 1894, 65, 324.
[27] Schaarschmidt and Hofmeier, *Ber.*, 1925, 58B, 1047.
[28] Klingstedt, *Ber.*, 1925, 58B, 2363.
[29] *Bull. acad. sci. U.S.S.R., Classe sci. math. nat.*, 1931, 1123; *Chem. Abs.*, 1932, 26, 3238.

The action of ***nitrogen pentoxide*** on ethylene and related hydrocarbons has been studied by Demyanov.[80] Glycol nitrates and addition products, in which nitrogen is linked to carbon, were formed. Tetramethylethylene gave three crystalline addition compounds: $C_6H_{12}N_2O_6$, $C_6H_{12}N_2O_5$, and $C_6H_{12}N_2O_4$, which were reduced to pinacol, glycolamine and diamine, respectively. No crystalline substances could be isolated from the products of the reaction with ethylene but the nitrate was detected by its explosive character, and diaminoethylene, $(CH_2NH_2)_2$, and glycolamine were obtained after reduction. This seemed to indicate the presence of $C_2H_5N_2O_6$. It was observed also that nitrogen pentoxide added easily to cyclohexene. In addition to the nitric esters, which were the main reaction products in each instance, dinitro-compounds, dinitro-alcohols, and nitro-nitrates were obtained.

Demyanov suggested that the colored nitroso-compounds may be intermediate reaction products, as follows:



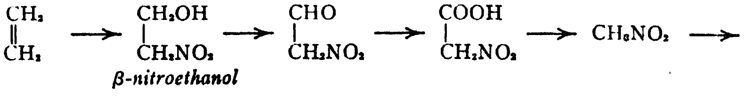
$$\underset{NO}{(CH_3)_2C}\text{—}\underset{NO_2}{C(CH_3)_2} + O \longrightarrow \underset{NO_2}{(CH_3)_2C}\text{—}\underset{NO_2}{C(CH_3)_2}$$

$$\underset{NO}{(CH_3)_2C}\text{—}\underset{ONO_2}{C(CH_3)_2} + O \longrightarrow \underset{NO_2}{(CH_3)_2C}\text{—}\underset{ONO_2}{C(CH_3)_2}$$

Haines and Adkins[81] observed no reaction between nitrogen pentoxide and ethylene, and obtained no crystalline substances from tetramethylethylene or cyclohexene. Stilbene formed addition compounds, and a flame hot enough to melt platinum was produced by the reaction of nitrogen pentoxide with a mixture of pentenes.

Since the nitrosates are readily split by heating with concentrated hydrochloric acid to yield fatty acids, it has been proposed to use them in the determination of the constitution of olefins.[82] From a technical point of view, however, the nitrosates and nitrosites thus far have been of little interest.

The action of ***nitric acid*** upon olefins usually results in violent oxidation reactions, but in the case of ethylene two well-defined reaction products have been isolated. Thus, McKie[83] considered that the reaction occurs in accordance with the following:



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \longrightarrow \begin{matrix}CH_2OH\\ |\\ CH_2NO_2\end{matrix} \longrightarrow \begin{matrix}CHO\\ |\\ CH_2NO_2\end{matrix} \longrightarrow \begin{matrix}COOH\\ |\\ CH_2NO_2\end{matrix} \longrightarrow CH_3NO_2 \longrightarrow$$

β-nitroethanol

$CH(NO_2)=NOH \longrightarrow CH_2=(NO_2)_2 \longrightarrow C(NO_2)_2=NOH \longrightarrow CH(NO_2)_3$

nitroform

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[80] *Compt. rend. acad. sci. U.S.S.R.*, 1930A, 447; *Chem. Abs.*, 1931, 25, 1215.
[81] *J.A.C.S.*, 1925, 47, 1419.
[82] Jegorov, *J. prakt. Chem.*, 1912, (2) 86, 521; *Chem. Soc. Abs.*, 1913, 104 (1), 153.
[83] *J.C.S.*, 1927, 962.

Of the above substances only β-nitroethanol and nitroform were definitely isolated, the yield of nitroform varying with the concentration of the nitric acid. Side reactions, mainly oxidation to oxalic acid, may account for 30 to 40 per cent of the ethylene. These can be partly inhibited by the addition of slightly less than 1 per cent of mercuric nitrate, which accelerates the reaction and increases the yield of nitroform.

When ethylene is passed into a well-cooled mixture of nitric and sulphuric acids an oil separates which consists of a mixture of ethylene glycol dinitrate and β-nitroethyl nitrate.[34] Separation of these compounds may be effected by fractional distillation or the mixture may be used directly as a substitute for nitroglycerol in low-freezing dynamites. Propylene and butylene form corresponding derivatives.

Forrest and Meigs [35] described the preparation of resinous materials by the action of dilute nitric acid on distillates containing high proportions of unsaturated hydrocarbons. Nitric acid is added in small portions to the distillate maintained at about 93° C. (200° F.) and the resins are separated by cooling. They may be combined or mixed with pyroxylin in all proportions in the presence of a mutual solvent.

DOUBLE COMPOUNDS OF OLEFINS WITH INORGANIC SALTS

Many of the olefins form double compounds with inorganic salts or inorganic salt solutions in water, alcohol or other solvents containing hydroxyl groups. Among the inorganic substances which appear to be capable of combining with olefins are aluminum, silver, cuprous, mercuric, platinous and ferrous salts. Many of these double compounds have been prepared in a crystalline condition [36] while others are known only in solution. The majority seem to be ordinary molecular compounds, easily resolved into their components. Thus, aqueous solutions of cuprous and silver salts absorb large quantities of ethylene at low temperatures, but the ethylene is expelled on raising the temperature. The use of aqueous solutions of silver nitrate at 10° C. for absorbing ethylene from gases has been described by Horsley.[37] The ethylene is regenerated by warming the solution to 50° to 70° C. Curme [38] suggested a similar method in which ethylene is absorbed in a solution of a mercury salt, e.g., mercuric sulphate, from which it is easily expelled by heating.

Of the double compounds of olefins with inorganic salts, those with mercury have received the most attention. The gaseous olefins readily form complex mercury compounds [39] from which the olefins may be regenerated by the action of hydrochloric acid. The corresponding reaction of the higher olefins is frequently accompanied by reduction of the mercuric salt to the mercurous salt with simultaneous oxidation of the hydrocarbon. When alcoholic solvents are employed, the solvent also enters into the reaction and the final products contain an alkoxyl group.

The compounds of mercuric acetate with cyclohexene, methylcyclohexene and the terpenes were described by Tausz.[40] He also succeeded in preparing double compounds of amylene and hexene.[41] Hugel and Hibou[42] found that for each olefin the addition compounds with mercuric salts have variable compositions according to the experimental conditions. It was also observed that while the higher olefins react slowly or not at all in aqueous solution (although the reaction is accelerated in alcoholic solution[43]), olefins of the type of tetramethylethylene and the tetra-alkylethylenes as a class definitely do not react.

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[34] Woodbury, U. S. Patent 1,485,003, Feb. 26, 1924; assigned to E. I. du Pont de Nemours and Co., Inc.; *J.S.C.I.*, 1924, **43**, 495B.

[35] U. S. Patent 1,305,790, June 3, 1919; Barber Asphalt Paving Co. See also Chapter 47.

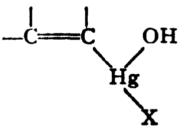
[36] See for example, Birnbaum, *Ann.*, 1868, **145**, 69; Zeise, *Pogg. Ann.*, 1884, **21**, 497, 542; 1890, **40**, 234; Henderson and Gangloff, *J.A.C.S.*, 1916, **38**, 1382.

[37] British Patent 291,186, 1927; assigned to Synthetic Ammonia and Nitrates, Ltd. See also purification of ethylene-containing gases, Chapter 4.

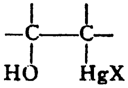
[38] U. S. Patent 1,315,541, Sept. 9, 1919; assigned to Union Carbide Co.; *J.S.C.I.*, 1919, **38**, 847A.

[39] Hofmann and Sand, *Ber.*, 1900, **33**, 1340, 1353, 2692; Sand, *Ber.*, 1901, **34**, 1385; *Ann.*, 1903, **329**, 135; Denigès, *Compt. rend.*, 1898, **126**, 1145, 1868; *Chem. Soc. Abs.*, 1898, **74** (1), 546; *ibid.*, 1899, **76** (1), 22.

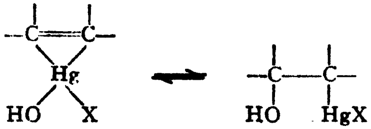
The compounds of ethylene with mercury salts have been most investigated. Considerable controversy has raged on the question of the constitution of these compounds. Manchot[44] regarded them as molecular addition compounds represented by structure I (see below) though the more common theory is that these compounds are true addition compounds of type II. On the other hand, Sand[45] has represented them as an equilibrium mixture between a molecular addition product and the ordinary type of addition compound (type III).



Type I



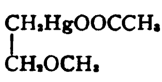
Type II



Type III

The merits of the three structures have been rather fully discussed by Adams, Roman and Sperry.[46] At the present time the evidence seems to show that these compounds are true addition compounds of type II. This is supported by the work of Adams, Roman and Sperry on the addition of mercuric salts to o-allylphenol and the preparation of optically active mercury compounds from olefins of the type $RR^1C{=}CRR^1$ by Sandborn and Marvel.[47]

In the formulas given above, representing the mercury addition compounds, an alkyl group may replace a hydrogen atom in the hydroxyl group when alcoholic solvents are used instead of water. Thus, mercuric acetate in methanol solution readily combines with ethylene to yield the ether,[48]



$$\begin{array}{l}CH_2HgOOCCH_3\\ |\\ CH_2OCH_3\end{array}$$

It is probable that some of these double compounds with mercuric salts will be employed in the future for the preparation of various organic substances. Schoeller[49] has described the preparation of $\beta\beta'$-dihalogeno-ethers therefrom. On shaking an aqueous suspension of mercuric sulphate vigorously with ethylene under pressure, the gas is absorbed rapidly with the formation of soluble dimercurated compounds. On addition of aqueous potassium iodide to the filtered liquid, $\beta\beta'$-bisiodomercuridiethyl ether is obtained in 95 per cent yield together with a little β-hydroxy-β'-iodomercuridiethyl ether. By the action of iodine in warm ethyl acetate, the former substance is converted into $\beta\beta'$-di-iododiethyl ether, a liquid boiling at 93°-94° C. at 1 mm. pressure. The dichloro- and dibromo-derivatives may be similarly prepared and propylene and higher olefins react in an analogous manner. The reaction may be represented as

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[40] *Chem.-Ztg.*, 1913, 37, 1023. See also Balbiano, *Ber.*, 1915, 48, 394.

[41] Technische Hochschule Karlsruhe, Thesis, 1911; see Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 504.

[42] *Chimie et Industrie*, Spec. No., Feb. 1929, 296; *Chem. Abs.*, 1929, 23, 3898.

[43] Schönbein, *J. prakt. Chem.*, 1855, (1) 66, 282.

[44] *Ber.*, 1920, 53, 984.

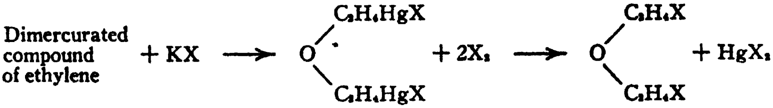
[45] *Ann.*, 1903, 329, 135; *Chem. Soc. Abs.*, 1904, 86 (1), 22.

[46] *J.A.C.S.*, 1922, 44, 1781.

[47] *J.A.C.S.*, 1926, 48, 1409.

[48] Schoeller, Schrauth and Essers, *Ber.*, 1913, 46, 2864.

[49] German Patent 437,159, 1923; *Brit. Chem. Abs.* B, 1927, 459.



$$\text{Dimercurated compound of ethylene} + KX \longrightarrow O\begin{cases}C_2H_4HgX\\C_2H_4HgX\end{cases} + 2X_2 \longrightarrow O\begin{cases}C_2H_4X\\C_2H_4X\end{cases} + HgX_2$$

in which X is a halogen atom. A more complete investigation of such reactions would undoubtedly be valuable.

Kharasch[49a] suggested the use of mercuriated olefins or their chlorine, cyanogen or hydroxyl derivatives in the preparation of seed disinfectant compositions.

OTHER REACTIONS OF OLEFINS

The *hydrogenation* of olefins has been frequently employed for the preparation of some of the higher liquid paraffins. The reaction, within certain limits of temperature, is reversible, hydrogenation being favored by low temperatures and dehydrogenation by higher temperatures. Catalysts for the hydrogenation of olefins include metallic nickel, cobalt and copper, as well as platinum and palladium. A comprehensive investigation of the two latter materials in the hydrogenation of numerous unsaturated substances at 2 to 3 atmospheres pressure of hydrogen at 25° C. has been made by Kern, Shriner and Adams.[50]

The direct combination of *hydrogen sulphide* with olefins should proceed according to

$$C_nH_{2n} + H_2S \longrightarrow C_nH_{2n+1}SH$$

and lead to the production of mercaptans. Nisson and Mandelbaum[51] and Johansen[52] have described the formation of mercaptans in this manner. Both subjected vapors containing olefins and hydrogen sulphide to the action of an adsorptive catalyst (fuller's earth or silica gel). Johansen[53] also suggested that mercaptans be obtained by the reaction between unsaturated hydrocarbons and hydrogen sulphide at ordinary temperatures in the presence of sulphuric or other inorganic acids.

The combination of hydrogen sulphide with ethylene, propylene, butene-1 and amylene at high temperatures (650° to 725° C.) in the presence of silica gel as the contact material has been studied by Mailhe and Renaudie.[54] A wide variety of products was obtained, including hydrogen, methane, saturated and unsaturated hydrocarbons, mercaptans, thioethers, thiophene and its homologues, and carbon disulphide. The thiophenes and thioethers were derived from the progressive decomposition of the mercaptans initially formed. The proportion of carbon disulphide increased with rising reaction temperature. Evidently, in order to obtain good yields of mercaptans, lower temperatures and catalysts more active than those used are necessary.

Duffey, Snow and Keyes[54a] tested the effect of various catalysts, time of contact, and temperature on the reaction of olefins with hydrogen sulphide. Equal volumes of the gases were passed through pyrex glass tubes containing catalyst at 200° to 300° C. Both ethylene and propylene formed mercaptans, with negligible proportions of alkyl sulphides. Maximum conversion of propylene was obtained at 200° C. with a low rate of flow of the gas through the tube and with nickel on kieselguhr or phosphoric acid on charcoal as catalyst. Ethylene gave best results at 250° C. with nickel on kieselguhr.

[49a] U. S. Patent 1,820,001, Aug. 18, 1931; assigned to E. I. duPont de Nemours and Co.; *Brit. Chem. Abs.* B, 1933, 246.

[50] *J.A.C.S.*, 1925, 47, 1147. A complete survey of this field can be found in Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930.

[51] U. S. Patent 1,836,183, Dec. 15, 1931; assigned to Gray Process Corp.; *Chem. Abs.*, 1932, 26, 995.

[52] U. S. Patent 1,836,171, Dec. 15, 1931; assigned to Gray Process Corp.; *Chem. Abs.*, 1932, 26, 995.

[53] U. S. Patent 1,836,170, Dec. 15, 1931; assigned to Gray Process Corp.; *Chem. Abs.*, 1932, 26, 995.

[54] *Compt. rend.*, 1932, 195, 391; *Brit. Chem. Abs.* A, 1932, 928.

[54a] *Ind. Eng. Chem.*, 1934, 26, 91.

The direct addition of the disulphide group (–S–S–) to the double bond of styrene and amylene, which could not be effected with hydrogen sulphide, was accomplished by King and Wilkinson[55] by treating these hydrocarbons with hydrogen persulphides.

Keller[55a] prepared sulphurized hydrocarbon derivatives which can be used as insecticides by heating unsaturated hydrocarbons or their halogen, hydroxy or amino derivatives with sulphur, hydrogen sulphide or polysulphides. Thus, a trichlorinated hard paraffin wax may be heated to 140° C. under pressure with potassium hydroxide saturated with hydrogen sulphide.

On passing a mixture of ethylene and acetylene at a high temperature over activated silica-gel mixed with pyrites, products containing thiophene and pyridic substances are said to result.[55b]

It has long been known that the introduction of a carbonyl, cyano, or similar group into an olefin molecule in a position adjacent to the double bond confers upon the resulting $\alpha\beta$-unsaturated ketone (nitrile or similar compound) remarkable powers of condensation with numerous reagents such as ammonia, amines, urea, semicarbazide, mercaptans and hydrogen cyanide. This activity has been regarded as due entirely to the combined ethylene-carbonyl (or ethylene-cyano) group. It is possible that many of the reactions of the ethylene-carbonyl group will be found to be possessed, to a lesser extent perhaps, by the simple olefins when the conditions for the combination of the latter substances have been carefully investigated. It is admitted, however, that in many cases combination appears to be extremely difficult to effect. Experiments on the direct combination of hydrogen cyanide, for example, with olefins including cyclohexene and styrene, have given uniformly negative results.[56]

Birckenbach and Linard[57] described the direct combination of iodine cyanate, prepared by the action of iodine on silver cyanate, with olefins to yield iodo-olefin isocyanates. Thus, cyclohexene in ether at —80° C. readily combines with this reagent to form 2-iodocyclohexylisocyanate (boiling point, 94° C. at 2 mm.) in 72 per cent yields.

It appears that certain "free" radicals, such as the cyanogen and thiocyanogen groups, can unite with olefins directly, provided the radical is generated in the nascent state. Kaufmann and Liepe[58] obtained combination of unsaturated hydrocarbons with "free" thiocyanogen in glacial acetic acid solution. The free thiocyanogen, which possesses haloid properties, was generated *in situ* by the action of bromine on a solution of lead thiocyanate:

$$Pb(CNS)_2 + Br_2 \longrightarrow PbBr_2 + (CNS)_2$$

Some formation of ordinary (bimolecular) thiocyanogen takes place.

[55] *J.A.C.S.*, 1932, 54, 3070.

[55a] German Patent 559,739. 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 730; addition to German Patent 557,245, 1930; *Chem. Abs.*, 1933, 27, 310. Reactions of alkali polysulphides with ethylene dichloride to produce rubber-like plastics have already been mentioned in Chapter 20.

[55b] I. G. Farbenindustrie A.-G., French Patent 679,540, 1929; *Chem. Abs.*, 1930, 24, 3867.

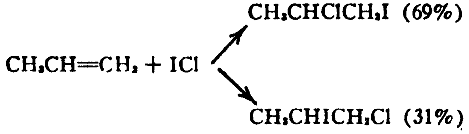
[56] Kolker and Lapworth, *J.C.S.*, 1925, 127, 309.

[57] *Ber.*, 1931, 64B, 961.

[58] *Ber.*, 1924, 57, 925.

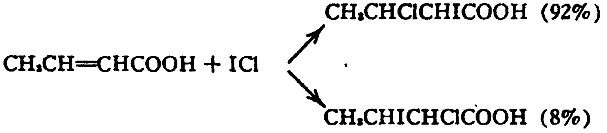
Mooney and Reid[59] showed that neither cyanogen nor cyanogen chloride or bromide react with ethylene at comparatively low temperatures (37° C.), but the reaction between cyanogen iodide and ethylene gives ethylene iodide and cyanogen.

Although iodine monochloride is a common reagent for determining the degree of unsaturation of many substances (e.g., vegetable oils), the manner in which it adds at the double bond has been investigated by only a few workers.[60] Ingold and Smith[61] observed that this substance reacts with the simple olefins to yield largely the α-iodo-compounds. For example, the reaction between propylene and iodine monochloride yields 69 per cent of α-iodo-β-chloro-propane and 31 per cent of α-chloro-β-iodo compound:



$$\begin{tikzcd}[row sep=small] & CH_3CHClCH_2I\ (69\%) \\ CH_3CH{=}CH_2 + ICl \arrow[ur] \arrow[dr] & \\ & CH_3CHICH_2Cl\ (31\%) \end{tikzcd}$$

In the case of olefins containing a substituted negative grouping, such as a phenyl, carboxyl, or sulphonic acid group, the iodine attaches itself to the carbon atom nearest the substitution. For crotonic acid, the addition can be represented by:



$$\begin{tikzcd}[row sep=small] & CH_3CHClCHICOOH\ (92\%) \\ CH_3CH{=}CHCOOH + ICl \arrow[ur] \arrow[dr] & \\ & CH_3CHICHClCOOH\ (8\%) \end{tikzcd}$$

The production of *acrylic acid* or its polymers by the direct vapor-phase combination of ethylene (or ethanol) with carbon dioxide has been described by the Röhm u. Haas A.-G.[62] The reaction is carried out under high pressure at high temperatures in the presence of ultraviolet light radiation (alone or with the silent electric discharge) and catalysts such as acidic gases (sulphur dioxide or oxides of nitrogen) or acid-reacting materials (e.g., acid salts of phosphoric acid or acid metallic oxides). By passing 26 grams of ethylene and 44 grams of carbon dioxide over silica gel or pumice impregnated with ferric phosphate at a temperature of 200° to 350° C. and a high gas velocity, yields of 10 per cent or more of acrylic acid are obtained. Longer heating periods and higher temperatures favor the formation of acrylic acid polymers.

Olefins react with formaldehyde, or better trioxymethylene, in an acetic-sulphuric acid medium to yield the diacetate of a glycol. This can then be hydrolyzed to the corresponding glycol in the usual manner. Such a procedure is applicable to the synthesis of 1,3-glycols of the aliphatic or hydroaromatic series.[63]

Unsaturated compounds obtained in the liquid sulphur dioxide extract from petroleum oils have been treated by Day[63a] with a 40 per cent solution of formaldehyde. A two-layer system was formed. The lower aqueous layer on evaporation left a resin, soluble in acetone and alcohol, which was said to be a substitute for shellac.

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[59] *J.C.S.*, 1931, 2597.

[60] For example, Erlenmeyer, *Ann.*, 1896, 289, 259; *Chem. Soc. Abs.*, 1896, 70 (1), 302. Michael, *J. prakt. Chem.*, 1899, (2) 60, 286, 409; *Chem. Soc. Abs.*, 1900, 78 (1), 321. Ingle, *J.S.C.I.*, 1902, 21, 591.

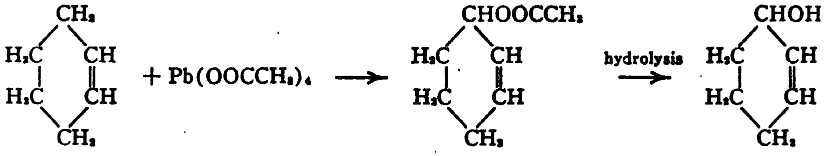
[61] *J.C.S.*, 1931, 2742.

[62] German Patent 553,179, 1929; *Chem. Abs.*, 1932, 26, 4610.

[63] Soc. des usines chim. Rhône-Poulenc, French Patent 717,712, 1930; *Chem. Abs.*, 1932, 26, 2752.

[63a] U. S. Patents 1,933,715 and 1,933,716, Nov. 7, 1933; assigned to Universal Oil Products Co.

Criegee and Schoeller [64] have suggested a method for the conversion of cyclic monolefins into unsaturated alcohols (or their esters) by treatment with an organic salt of tetravalent lead (e.g., lead tetra-acetate). As an illustration, 45 grams of cyclohexene are stirred for several hours at 80° C. with 250 grams of lead tetra-acetate and 250 cc. of glacial acetic acid. The mixture is diluted with water, extracted with ether, and distilled under reduced pressure. The distillate contains 2-acetoxycyclohexene (boiling point, 68°-71° C. at 12 mm.), which can be hydrolyzed to cyclohexenol-2. The reaction, which is a type of oxidation, can be represented in the following manner:



In a similar manner menthenol acetate is obtained from menthene.

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[64] German Patent 550,704, 1930; assigned to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1932, 26, 4824.

Chapter 26

Polymerization of Monolefins and Diolefins. Production of Synthetic Rubber

Although, strictly speaking, the term polymerization is usually reserved to designate those reactions of a reversible nature in which the union of two or more molecules takes place (exemplified by the well-known acetaldehyde-paraldehyde equilibrium), the term is conveniently used, when applied to hydrocarbons, to cover all conversions into higher molecular weight hydrocarbons of the same carbon-hydrogen atomic ratio, irrespective of reversibility.[1] It appears that the polymerization reactions of hydrocarbons are either completely irreversible or only reversible within very narrow limits.

The power of polymerization is an inherent property of unsaturated hydrocarbons as a class, including monolefins, diolefins, acetylenes, and diacetylenes,[2] and is not possessed by typical saturated hydrocarbons, such as paraffins and cycloparaffins, or by aromatic hydrocarbons. Calculations based upon free-energy data,[3] and upon the Nernst approximation formula,[4] show that the simple monolefins are thermodynamically unstable below about 425° C. Above this temperature there is an increasing tendency for decomposition to occur.[5] The tendency for olefins to polymerize is greatest at lower temperatures and diminishes with rising temperature, a deduction in agreement with the observed highly exothermic character of such polymerizations. Although polymerization is favored by low temperatures, the reaction velocity is usually low under such conditions, hence catalysts are highly advantageous in bringing about low-temperature polymerizations. It is obvious that increased pressures favor polymerization of the gaseous olefins.

According to Tammann and Pape[6] the velocity of polymerization of liquid styrene, vinyl acetate and diolefins increases with increasing pressure more rapidly than in other reactions which occur in the liquid phase, but the form of the relationship between velocity coefficient and pressure varies with the individual hydrocarbon. Increase of pressure also reduces the temperature at which polymerization commences.

The polymerization of olefins may be brought about by heat alone, without the aid of catalysts, but the favorable influence of higher temperatures on reaction velocity is often counterbalanced by a diminishing thermodynamic tendency to polymerization, and an increasing tendency for cracking to occur (see Chapter 2). Although many examples of purely thermal polymerization are known, the initial polymerization products are almost always further decomposed with the production of hydrogen, paraffins, and hydrocarbons with carbon-hydrogen ratios which differ from those of the olefin. A combination of moderate heat and high pressure favors the polymerization of olefins in the gaseous phase. Perhaps the most striking feature of olefin polymerization reactions, however, is the variety of catalysts capable of accelerating them. These catalysts include not only acids (such as sulphuric and phosphoric acids), but aluminum chloride, ferric chloride, boron trifluoride, zinc chloride, sulphur chloride, and other metallic salts, as well as activated charcoal, silica gel, floridin, and other adsorbent earths. The activity of many of these catalysts is increased with increased pressures (on gaseous materials) and with temperatures not exceeding about 400° C. The polymerization of olefins is frequently both initiated and accelerated by certain forms of energy such as ultraviolet radiation, silent electric discharge, and α-radiation. Here again, however, as in the thermal polymerization of olefins, the initial polymerization products frequently undergo further degradation, polymerization and splitting, so that the main reaction becomes obscured by a host of secondary changes.

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[1] Condensation, on the other hand, is the union of two or more molecules with the splitting out of water, hydrogen chloride, or other substance to produce compounds which are usually not reconvertible by any simple method into the original molecules.

[2] The polymerization of acetylene and diacetylene homologues and derivatives is discussed in Chapter 28.

[3] Francis, *Ind. Eng. Chem.*, 1928, **20**, 277; Francis and Kleinschmidt, *Proc. Amer. Petr. Inst.*, 1930, **11**, 93.

[4] Sachanov and Tilicheev, *Ber.*, 1929, **62**, 658; *Neft. Khoz.*, 1929, **16**, 223; *Chem. Abs.*, 1929, **23**, 4807. See also Sachanen and Tilicheyev, "Chemistry and Technology of Cracking," translated by Boehtlingk, Brown, and Steik, Chemical Catalog Co., Inc., New York, 1932, 137.

[5] *Cf.* also Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., Inc., New York, 1932, 76.

[6] *Z. anorg. Chem.*, 1931, **200**, 113; *Brit. Chem. Abs.* **A**, 1931, 1239.

The products of polymerization of the simple monolefins differ greatly in physical and chemical properties, depending upon the conditions of polymerization and especially upon the catalyst used (if any). These products may vary, for example, from simple low-boiling dimers (substances with the same atomic proportions but with a molecular weight twice that of the parent substance) to viscous high molecular weight polymers, some of which have the appearance and consistency of heavy lubricants. Chemically, the fundamental initial stage of the polymerization is undoubtedly the formation of an olefin with twice the molecular weight of the original. Thus, in the case of ethylene, it has been shown that the first product of the polymerization is 1-butene, formed by the reaction

$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_3CH_2CH{=}CH_2$$

irrespective of whether heat treatment,[7] silent electric discharge,[8] or catalysts (such as aluminum chloride or boron trifluoride),[9] are employed. Unless conditions are so arranged that the 1-butene is removed rapidly from the sphere of reaction, it frequently undergoes further alteration. Many of the dimers and trimers of the butylenes and amylenes have been shown by numerous workers to be aliphatic olefins.

Although the initial stage of polymerization is undoubtedly the formation of a dimeric olefin, it does not usually stop at that point. Indeed, under the powerful polymerizing influence of such agents as aluminum chloride and boron trifluoride, it usually proceeds much farther, so that very high molecular weight hydrocarbons are produced. The polymerization to higher olefins may also be followed by ring closure of the higher olefins with the formation of saturated cycloparaffins of the formula C_nH_{2n}. The isomerization of the higher olefins to the corresponding cycloparaffins is possible from a thermodynamic standpoint at temperatures below about 400° C. This isomerization of olefins to cycloparaffins was observed by Ipatiev[10] in his work on ethylene. Other reactions may also degrade the higher olefins produced by the straight polymerization, such as the splitting off of paraffin hydrocarbon residues which occurs when aluminum chloride is employed.[11]

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[7] Hague and Wheeler, *J.C.S.*, 1929, 378; Pease, *J.A.C.S.*, 1930, 52, 1158; see Chapter 2.

[8] Mignonac and Vanier deSaint-Aunay, *Compt. rend.*, 1929, 189, 106; *Chem. Abs.*, 1929, 23, 4668; *cf.* polymerization of acetylene, *Compt. rend.*, 1929, 188, 959; *Chem. Abs.*, 1929, 23, 3437; see Chapter 9.

[9] Otto and Bub, German Patent 545,397, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 2990; I. G. Farbenindustrie A.-G., British Patent 326,322, 1929; *Brit. Chem. Abs.* B, 1930, 500.

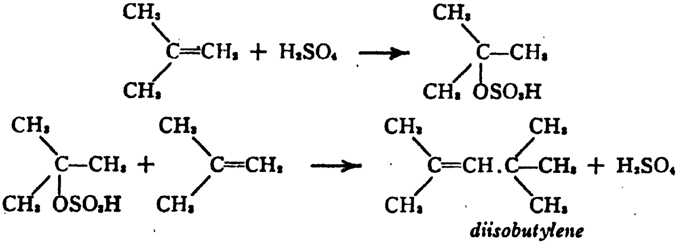
[10] *Ber.*, 1911, 44, 2978; see also Chapter 2.

In the polymerization of olefins under the influence of heat, pressure, or catalysts, the initial product appears to be a dimer containing one double bond. However, the dimer is not always a straight-chain olefin, since there is a tendency for the production of a branched carbon chain. This phenomenon may be due to the tendency of olefins to isomerize, under the influence of heat and catalysts, to the corresponding iso-olefin. Thus, as will be mentioned later, isopropylethylene is isomerized by heat and catalysts to the isomeric trimethylethylene. An example of the isomerization of a straight-chain olefin to a branched-chain dimer is provided by the work of Hugel and Cohn[12] on hexadecene. When heated to 300° to 400° C. at pressures above 15 atmospheres this hydrocarbon undergoes polymerization to the dimer, $C_{32}H_{64}$, and the trimer, $C_{48}H_{96}$. A study of the dimeric hydrocarbon fraction led to the conclusion that it contained one solid monolefin of the formula $C_{32}H_{64}$ containing no side chain and with the ethylene bond located in the middle of the chain, together with liquid dimers ($C_{32}H_{64}$) with branched chains. Less of the solid dimer was formed at 400° C. than at 300° C., a result which supports the isomerization theory given above, since more of the straight-chain dimer can be expected to isomerize to branched-chain dimers at the higher temperature.

MECHANISM OF POLYMERIZATION

Although the phenomenon of polymerization is of great importance because of the valuable products produced from relatively simple raw materials, there is perhaps no subject in chemistry more difficult, both experimentally and theoretically, or so little understood. Clark[13] has distinguished two possible broad types of polymerization: (1) Simple kinetic molecules associate to form a singly acting unit by the action of residual or secondary valence forces, and (2) monomeric molecules or residues combine with each other under the influence of primary valence forces to form chains of indefinite length.

The polymerization of olefins by sulphuric acid was considered by Kondakov[14] to proceed through the intermediate formation of an alkylsulphuric acid which may then condense with another molecule of olefin, thus:



The polymerization of olefins by anhydrous metallic halides, such as boron trifluoride or aluminum chloride, undoubtedly involves the intermediate formation of organometallic complex compounds, which are usually obtained in the form of dark pasty masses insoluble in light petroleum.[15] The mechanism of polymerization in other cases, for example, during thermal treatment or under the influence of light or silent electric discharge, is still less understood. Brooks [16] stated that polymerization, in common with certain other phenomena, is really intimately connected with the nature of valence itself and that ordinary graphic formulas, in themselves, only inadequately furnish a plausible explanation. It is extremely likely, however, that as a preliminary to the addition of one olefin molecule to another, activation of the molecule occurs with the production of a reactive "free" radical with two free linkages.[17] The possible formation of free radicals has been definitely proved by positive-ray research on hydrocarbons and by the work of Paneth and Hofeditz [18] on the free methyl radical.

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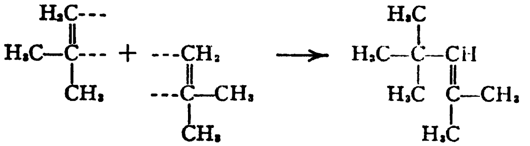
[11] Stanley, *J.S.C.I.*, 1930, 49, 349T; see Chapter 6.

[12] *Ann. combustibles liquides*, 1932, 7, 239; *Chem. Abs.*, 1932, 26, 5543.

[13] *Ind. Eng. Chem.*, 1929, 21, 128.

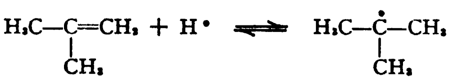
[14] *J. Russ. Phys.-Chem. Soc.*, 1893, 24, 309; *Chem. Soc. Abs.*, 1893, 64, 382; *J. prakt. Chem.*, 1896, (2) 54, 442, 454; *Chem. Soc. Abs.*, 1897, 72 (1), 209; see also Brooks, "Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, 1922, 210; *J. Inst. Pet. Tech.*, 1928, 14, 752.

A graphical interpretation of polymerization has been proposed on the basis of Thiele's theory, according to which the doubly linked carbon atoms possess partial valences or "residues of free affinity." [19] The further assumption is made that the molecules contain a mobile or labile hydrogen atom which shifts from one molecule to another. The polymerization of isobutylene may then be expressed graphically:



$$H_3C{-}\underset{\underset{CH_3}{|}}{\overset{\overset{H_2C---}{\|}}{C}}{---} + \underset{\underset{\underset{CH_3}{|}}{---C{-}CH_3}}{\overset{---CH_2}{\|}} \longrightarrow H_3C{-}\underset{\underset{H_3C}{|}}{\overset{\overset{H_3C}{|}}{C}}{-}\underset{\underset{\underset{\underset{H_3C}{|}}{C{-}CH_3}}{\|}}{CH}$$

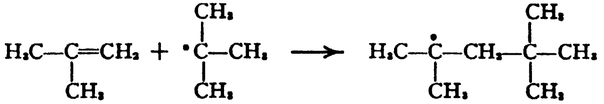
Whitmore [19a] proposed a theory for the mechanism of polymerization based upon the catalytic effect of hydrogen ions present in the reaction mixture. With isobutylene as an example, the first step in the reaction is the addition of a hydrogen ion to the olefin:



$$H_3C{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H^{\bullet} \rightleftharpoons H_3C{-}\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}{-}CH_3$$

(I) (II)

producing a tertiary butyl group (II) which is positively charged. In the same way that a hydrogen ion reacted with the olefin, the positively charged tertiary butyl group can now react with a molecule of the olefin (I) to yield the intermediate III, which is also positively charged:



$$H_3C{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2 + {}^{\bullet}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \longrightarrow H_3C{-}\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3$$

(III)

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[15] Stanley, *loc. cit.*; Szayna, *Przemysl Chem.*, 1928, 12, 637; *Chem. Abs.*, 1929, 23, 1384.

[16] *J. Inst. Pet. Tech.*, 1928, 14, 746; "Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, 1922, 210.

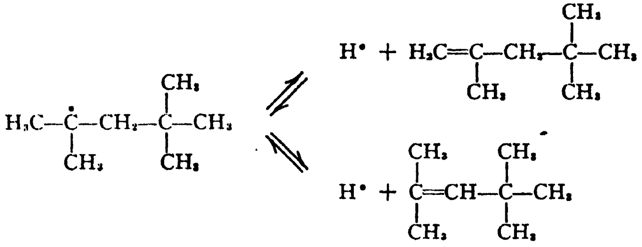
[17] Hurd and Spence, *J.A.C.S.*, 1929, 51, 3561; see Chapter 2. Various mechanisms of polymerization reactions are summarized by Milas (*Chem. Reviews*, 1932, 10, 295; *Chem. Abs.*, 1932, 26, 3432; *cf.* Chalmers, *Can. J. Research*, 1932, 7, 113; *Chem. Abs.*, 1932, 26, 5480).

[18] *Ber.*, 1929, 62, 1335.

[19] See Morrell, *Ind. Eng. Chem.*, 1927, 19, 794; Brooks, *J. Inst. Pet. Tech.*, 1928, 14, 750; *cf.* Whitby and Katz, *J.A.C.S.*, 1928, 50, 1160 (polymerization of indene); McCubbin and Adkins, *J.A.C.S.*, 1930, 52, 2547 (polymerization of isobutylene); Stobbe and Posnjak, *Ann.*, 1909, 371, 287; *Chem. Abs.*, 1910, 4, 2120 (polymerization of styrene).

[19a] ***Ind. Eng. Chem.*, 1934, 26, 94.**

The intermediate III can now either undergo further condensation, or, by loss of a hydrogen ion, form a double-bonded molecule:



$$H_3C-\overset{\bullet}{C}(CH_3)-CH_2-C(CH_3)_2-CH_3 \rightleftharpoons \begin{cases} H^{\bullet} + H_2C{=}C(CH_3)-CH_2-C(CH_3)_2-CH_3 \\ H^{\bullet} + (CH_3)_2C{=}CH-C(CH_3)_2-CH_3 \end{cases}$$

The hydrogen ions regenerated in this change can add to the olefins present and start the cycle again.

In the homologous series of olefin hydrocarbons, the tendency to polymerize increases from ethylene upwards and is at a maximum with the pentenes and hexenes. Structural differences in isomers exert, however, a very marked influence on the ease of polymerization. In general the iso-olefins such as isobutylene and trimethylethylene are more readily polymerized than the straight-chain members. The introduction of electronegative atoms or groups (such as halogen atoms or phenyl groups) into the olefin hydrocarbon molecule very greatly increases the tendency to polymerization.[20] Thus, vinyl halides and styrene are polymerized with very great ease while the parent olefin, ethylene, is relatively resistant to polymerization.

The di- and trimeric polymerization products of the simple olefins are far less easily polymerized than the parent hydrocarbon and show an increasing stability not only as regards polymerization but also against bromine addition and combination with sulphuric acid.

In the following account, a survey has been made of the work on the polymerization of the lower olefins. In previous chapters some mention has been made of the action of heat, sulphuric acid, and aluminum chloride[21] on the lower olefins, so that only brief reference to these reactions, in so far as they relate to the general question of polymerization, need be made. Certain catalysts, however, which have not been previously included, are described in this section.[22]

ETHYLENE

Although ethylene is more resistant to polymerization than its immediate homologues, it can be polymerized under the influence of various agents. The non-catalytic thermal decomposition of ethylene, though complex, results initially, as has been mentioned, in the production of butylene at comparatively low temperatures. Hague and Wheeler[23] found that, on heating ethylene under normal pressure in silica bulbs for 3 hours, the production of butylene was at a maximum at 500° C., corresponding to a content of higher olefins in the resulting gas of 13.7 per cent. Similarly, Pease[24] concluded that the non-catalytic thermal decomposition of ethylene at 400° to 600° C. first yields butylene, evidently by a chain reaction.

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[20] *Cf.* Parks and Huffman, *op. cit.*, 83.

[21] See Chapters 2, 6 and 14, respectively.

[22] The decomposition and polymerization of the olefins have been reviewed by Egloff, Schaad and Lowry, *J. Phys. Chem.*, 1931, 35, 1825. Farmer (*Sci. J. Roy. Coll. Sci.*, 1931, 1, 50; *Chem. Abs.*, 1933, 27, 2131) discussed the polymerizing capacities of olefins and butadienes.

[23] *J.C.S.*, 1929, 378.

[24] *J.A.C.S.*, 1930, 52, 1158.

On the other hand, Lenher[25] observed that considerable propylene was formed during the slow oxidation of ethylene with oxygen at temperatures of 400° C. and over and believed that the purely thermal polymerization of ethylene resulted initially in the formation of propylene and not butylene. Several mechanisms were suggested to explain this transformation, one of which involved the combination of a C_2H_4 molecule with a free CH_2 radical.

As might be expected, the thermal polymerization of ethylene is markedly accelerated by the application of pressure. Ipatiev[26] found that at 70 atmospheres in a steel autoclave and at temperatures above about 325° C., ethylene readily condensed to liquid hydrocarbons. Since the products consisted not only of higher olefins but also paraffins and cycloparaffins, simple polymerization had in this case been followed by splitting and ring-closure. The temperature of polymerization of ethylene under pressure is considerably reduced by the presence of catalysts such as zinc chloride.[27] With aluminum chloride the polymerization of ethylene under pressure takes place at as low as 0° C. and gives rise to a mixture of hydrocarbons, most of which are of high molecular complexity.[28] In a similar way the polymerization of compressed ethylene in the presence of boron trifluoride yields high molecular weight oils.[29] The action of anhydrous aluminum chloride and boron trifluoride on olefins has aroused interest chiefly in connection with the possible synthesis of lubricating oils.

The conclusions of Dunstan, Hague and Wheeler[30] on the polymerization of olefins, particularly ethylene, at pressures of 200 to 2000 pounds per square inch and temperatures of about 350° to 600° C. were as follows[31]: (1) The temperature range is lower (700° to 900° C.) for the pyrolysis of olefins than for paraffins, and the percentage conversion (36 to 40 per cent) is higher. (2) Under operating conditions at 150 pounds per square inch pressure, 575° C. appears to be the approximate temperature distinguishing polymerization from decomposition with ethylene. (3) A reduction in volume takes place in polymerization. (4) The liquid polymerization products are not aromatic and the yields approach the theoretical. The liquid, of which 86 per cent boils below 200° C., has a high antiknock value[32] (engine test, five-sixths that of benzene). (5) Products which vary from gaseous higher olefins to synthetic lubricating oils can be produced at will by control of temperature, pressure, contact surface, and time of contact.

Molten sodium has a polymerizing effect on ethylene at 150° C. Walker[33] obtained a colorless liquid polymer in this manner and the sodium was converted to sodium ethylene carbide. Ethylene is polymerized by iron at 360° C. to a colorless oil.

The kinetics of the thermal polymerization of ethylene under pressure has been studied by Pease,[34] who showed that at temperatures of 350° to 500° C. in a static system at pressures up to 10 atmospheres, the reaction is roughly bimolecular and has an activation energy of about 35,000 calories per mole.

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[25] *J.A.C.S.*, 1931, **53**, 3752.

[26] *Ber.*, 1911, **44**, 2978.

[27] Ipatiev and Routala, *Ber.*, 1913, **46**, 1748.

[28] Stanley, *loc. cit.* Nash, Stanley and Bowen, *J. Inst. Pet. Tech.*, 1930, **16**, 830; *Proc. Third Internat. Conf. Bituminous Coal*, 1931, 928. Szayna, *loc. cit.* Hunter and Yohe (*J.A.C.S.*, 1933, **55**, 1248) advanced a theory of polymerization based on the electronic structures of aluminum chloride and olefins.

[29] Otto, *Brennstoff-Chem.*, 1927, **8**, 321; *Brit. Chem. Abs.* **B**, 1927, 930; see section on boron fluoride.

[30] *J.S.C.I.*, 1932, **51**, 131T.

[31] *Cf.* their previous work on pyrolysis of hydrocarbons to give aromatic hydrocarbons (*J.S.C.I.*, 1931, **50**, 313T) summarized in Chapter 5.

[32] *Cf.* Morgan, Ingleson and Taylor, *Petroleum Times*, 1931, **24**, 1024; *Chem. Abs.*, 1932, **26**, 289,

[33] *J. Phys. Chem.*, 1927, **31**, 961; *Chem. Abs.*, 1927, **21**, 3011; see Chapter 2,

[34] *J.A.C.S.*, 1931, **53**, 613.

Ramage [35] proposed to effect the polymerization of ethylene to butylene merely by compressing this gas into kerosene or some other heavy hydrocarbon solvent under a pressure of 80 to 200 pounds per square inch, at about 0° C., and recovering the polymerization products from the charged solvent by distillation. Besides butylene, the distillate was reported to contain small amounts of amylene, octylene, and decylene. The polymerization of olefins with anhydrous aluminum or boron halides has been accelerated with certain double compounds of the halide, for example, ansolvo-acids [36] or the double complexes of aluminum halides with organic compounds such as nitrobenzene, nitromethane, or ketones.[37]

Ethylene and its homologues are also polymerized by heating them under pressure without catalysts but in the presence of an inert liquid, such as a mineral or vegetable oil.[38] For example, ethylene is heated with paraffin oil to 420° C. under 45 atmospheres pressure to yield liquid hydrocarbons.

Polymerization in the vapor state of monolefins having 2 to 5 carbon atoms, at 40° to 300° C. in the presence of volatilizable inorganic halides, such as those of aluminum, tin, antimony, zinc, copper, or iron, is stated to yield higher liquid olefins when the contact time is 1 to 65 seconds.[39] The polymerization of ethylene to butylene can be accomplished by passing a slow stream of that gas over a catalyst of active charcoal containing 1 per cent of cobalt at 200° C., according to Schuster.[40]

Other catalysts are also capable of polymerizing ethylene, especially under pressure. Ethylene is fairly stable in the presence of sulphuric or ethylsulphuric acids at temperatures below 100° C. at ordinary or moderate pressures, but at high pressure some tendency to polymerization is observable. This tendency is greatly increased by the addition to the sulphuric acid of metallic salts such as cuprous and mercurous salts,[41] particularly the latter.[42]

The photochemical polymerization of ethylene in ultraviolet light from a mercury lamp was observed by Berthelot and Gaudechon [43] to yield a liquid which boils below 100° C. and has an odor of rancid fat. Similar results were also obtained by Landau,[44] but Bates and Taylor [45] attributed this polymerization not to the influence of ultraviolet light *per se* but to the agency of excited mercury atoms.

The polymerization of ethylene under the influence of the silent electric discharge was studied by Mignonac and Vanier deSaint Aunay,[46] who found that on subjecting ethylene under conditions such that the products of the reaction were

[35] U. S. Patent 1,527,079, Feb. 17, 1925; assigned to International Color and Chemical Co., Inc.; *Chem. Abs.*, 1925, **19**, 1710.

[36] Neutral molecules which combine with a solvent increasing its acidity by forming complex anions are called "ansolvo-acids" by Meerwein (*Ann.*, 1927, **455**, 227; *Brit. Chem. Abs.* **A**, 1927, 836), in extension of Werner's term "anhydro-acids." The most strongly acting ansolvo-acid studied was boron trifluoride. Boron trifluoride-acetic acid which boils at 59° C. at 13 mm. is as strong as sulphuric acid.

[37] Bataafsche Petroleum Maatschappij, British Patent 358,068, 1931; *Brit. Chem. Abs.* **B**, 1932, 172. French Patent 716,159, 1931; *Chem. Abs.*, 1932, **26**, 2197.

[38] Bataafsche Petroleum Maatschappij, British Patent 331,186, 1929; *Chem. Abs.*, 1931, **25**, 114.

[39] I. G. Farbenindustrie A.-G., British Patent 372,321, 1931; *Brit. Chem. Abs.* **B**, 1932, 714.

[40] German Patent 559,736, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 736.

[41] De Montmollin, *Bull. soc. chim.*, 1916, (4) **19**, 242; Damiens, *Chimie et industrie*, Special No. 208, May 1923; *Chem. Abs.*, 1923, **17**, 3094; *Bull. soc. chim.*, 1923, (4) **33**, 71; Böeseken and Max, *Rec. trav. chim.*, 1929, **48**, 486; *Chem. Abs.*, 1929, **23**, 2929; see Chapter 50.

[42] Stanley, *J.S.C.I.*, 1930, **49**, 349T.

[43] *Compt. rend.*, 1910, **150**, 1171; *Chem. Soc. Abs.*, 1910, **98** (1), 349.

[44] *Compt. rend.*, 1912, **155**, 403; *Chem. Abs.*, 1912, **6**, 3239.

[45] *J.A.C.S.*, 1927, **49**, 2438; *Proc. Nat. Acad. Sci.*, 1926, **12**, 714.

[46] *Compt. rend.*, 1929, **189**, 106; *Chem. Abs.*, 1929, **23**, 4668.

rapidly withdrawn from the reaction zone, the primary product was 1-butene from which 1-hexene was formed, thus:

$$(1)\ CH_2{=}CH_2 + H.CH{=}CH_2 \longrightarrow CH_3.CH_2.CH{=}CH_2$$

$$(2)\ CH_3.CH_2.CH{=}CH_2 + H.CH{=}CH_2 \longrightarrow CH_3.CH_2.CH_2.CH_2.CH{=}CH_2$$

However, if the products of reaction are not removed, ethylene yields a complex mixture of saturated and unsaturated hydrocarbons.

By the action of the silent discharge on ethylene, Collie[47] obtained a mixture of liquid hydrocarbons, boiling from 60° C. upwards and containing C_nH_{2n} hydrocarbons with 6 to 15 carbon atoms and in which was also indicated the presence of cycloparaffins. Demyanov and Prianischnikov,[48] with a silent discharge of 13,000 volts on ethylene, obtained liquid unsaturated hydrocarbons from C_6H_{12} upwards. The later work of Prianischnikov[49] on isobutylene showed that the process is not merely a simple polymerization but is accompanied by a splitting out and a redistribution of hydrogen atoms. Similar results have been reported by Stratta and Vernazza[50] on exposure of ethylene to the silent discharge.

The action of alpha-rays from radon (radium emanation) on the polymerization of ethylene and acetylene has been studied by Lind, Bardwell and Perry.[51]

POLYMERIZATION OF OLEFINS WITH BORON FLUORIDE

Although boron fluoride (BF_3) was first prepared by Gay-Lussac and Thénard[52] in 1808, its possibilities did not attract commercial attention until about 1925. It was first prepared by heating a mixture of 1 part boric oxide (B_2O_3) with 2 parts of fluorspar (fluorite, substantially CaF_2) in a closed gun barrel in an inclined position to white heat. Later, it was made by Davy[53] by gently heating 1 part boric acid with 2 parts of fluorspar and 12 parts of sulphuric acid. The direct synthesis of boron fluoride from its elements was accomplished by Moissan[54] in 1904. The product obtained from boric acid, fluorspar and sulphuric acid[55] melted at —127° C. and boiled at —101° C., but the synthetic product melted at —126° C. and boiled at —99° C. According to Ruff[56] and his co-workers, boron fluoride usually contains silicon fluoride as an impurity. They found that a sample containing 1.7 per cent of silicon tetrafluoride had a melting point of —128° C. and a boiling point of —101° C. at 760 mm. pressure. Boron trifluoride, which has now come into some prominence, can be produced by heating a mixture of a fluoride and boric acid or a borate, with fuming sulphuric acid or, alternatively, boric acid can be treated with fluorosulphonic acid.[57]

Butlerov and Gorianov[58] appear to have been the first to observe the polymerizing action of boron fluoride. They found that this material did not polymerize ethylene even at 200° C. but that propylene and butylene, on the other hand, were polymerized very readily even at room temperature. They stated that propylene, in the presence of boron fluoride, was polymerized to products more complex than a trimer at room temperature but Sowa, Hinton and Nieuwland[59] observed no such action, though their experimental conditions were entirely different.

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[47] *J.C.S.*, 1905, 87, 1540.

[48] *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 462; *Chem. Abs.*, 1927, 21, 3344.

[49] *Ber.*, 1928, 61, 1358.

[50] *Industria Chimica*, 1931, 6, 133; *Chem. Abs.*, 1931, 25, 4186.

[51] *J.A.C.S.*, 1926, 48, 1559, 1575.

[52] *Ann. chim. phys.*, 1808, 69, 204; see Gmelin, "Handbook of Chemistry" (translated by Watts). Cavendish Society, London, 1849, 2, 362.

[53] *Phil. Trans.*, 1812, 352; *Ann. chim. phys.*, 1812, 86, 178, see Gmelin, *loc. cit.*

[54] *Compt. rend.*, 1904, 139, 711; *J.S.C.I.*, 1904, 23, 1164; *Chem. Soc. Abs.*, 1905, 88 (2), 26.

[55] Moissan, *loc. cit.*

[56] Ruff, Braida, Bretschneider, Menzel and Plaut, *Z. anorg. Chem.*, 1932, 206, 59; *Brit. Chem. Abs.* A, 1932, 707.

[57] I. G. Farbenindustrie A.-G., French Patent 675,532, 1929; *Chem. Abs.*, 1930, 24, 2842; British Patent 324,016, 1928; *Brit. Chem. Abs.* B, 1930, 325.

[58] *Ann.*, 1873, 169, 147; *Ber.*, 1873, 6, 561; *Chem. Soc. Abs.*, 1873, 26, 873; Butlerov, *Ann.*, 1877, 189, 44; *Chem. Soc. Abs.*, 1878, 34, 121; *cf.* Gasselin, *Ann. chim. phys.*, 1894, (7) 3, 6; *Chem. Soc., Abs.*, 1895, 68 (1), 451.

As early as 1877 Landolph studied some of the reactions of boron fluoride with, for example, benzaldehyde,[60] ethylene,[61] amylene,[62] anethol,[63] and camphor.[64] Boron fluoride and ethylene reacted under light and heat at 30° C. to give an ethereal liquid boiling at 124° to 125° C. This liquid was called fluoborethylene or ethylene fluoboric acid and had the formula $C_2H_3.BF_2$. Amylene gave a yellow liquid which boiled at 160° C., and anethol ($CH_3.CH{=}CH.C_6H_4.O.CH_3$) was polymerized. The reaction of boron fluoride with acetonitrile was investigated by Patein[65]; and with methyl and ethyl alcohols, acetone, resorcinol, cetyl alcohol, glycol, glycerol, ethylene and amylene by Gasselin.[66]

Boron fluoride can be substituted for aluminum chloride in Friedel-Crafts syntheses, as well as in other reactions catalyzed by the latter compound. For example, Hofmann and Wulff[67] state that it can be used to effect condensations of aromatic hydrocarbons with aliphatic chlorides, the splitting of hydrocarbon oils[68] and the addition of hydrogen halides to olefins.

Nieuwland and his associates studied the reactions of boron fluoride with alcohols, acids, nitriles, esters, ethers, acid anhydrides and amides[69]; the preparation of esters from acetic and propionic acid-boron fluoride compounds and aliphatic alcohols[70]; the rearrangement of alkyl phenyl ethers under the influence of this compound[71]; the cleavage of ethers in the presence of organic acids and boron fluoride to give esters and alcohols[72]; and the condensation of propylene with phenol.[73] Meerwein[74] observed that boron fluoride added to olefins: formed a compound with dioxan; yielded dialcoholates with aliphatic alcohols; and combined with aliphatic acids and acetic anhydride. Accordingly, like aluminum chloride, boron fluoride can be used to effect many types of reactions, hence with its production on a commercial scale, it will probably attract even wider interest. This discussion must necessarily be limited, however, to the polymerizing action of boron fluoride on olefins, some examples of which have already been mentioned. Various other uses of this compound have likewise received some attention in other chapters.[75]

Otto[76] studied the polymerizing action of boron fluoride on ethylene and its immediate homologues under pressure. In the presence of this reagent isobutylene polymerized readily with the production of a water-white oil which boiled at 200° C. Propylene was more resistant, but, under high pressure, polymerization took place at ordinary temperatures with the formation of a yellow oil of high viscosity and with an initial boiling point of 120° C. at 15 mm., half of which distilled below 300° C. at this pressure. High molecular weight oils were also obtained from ethylene. Hofmann and Otto[77] found that this polymerization was accelerated by the use of finely divided metals such as nickel and that the double compounds of boron fluoride could likewise be used.

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[59] *J.A.C.S.*, 1932, 54, 3694.

[60] *Compt. rend.*, 1878, 86, 671, 1463; *Chem. Soc. Abs.*, 1878, 34, 482, 774; *Compt. rend.*, 1877, 85, 39; *Chem. Soc. Abs.*, 1877, 32, 864.

[61] *Compt. rend.*, 1878, 86, 671; *Chem. Soc. Abs.*, 1878, 34, 482; *Ber.*, 1880, 12, 1583; *Chem. Soc. Abs.*, 1880, 38, 28.

[62] *Ber.*, 1880, 12, 1583.

[63] *Compt. rend.*, 1878, 86, 601; *Chem. Soc. Abs.*, 1878, 34, 576.

[64] *Compt. rend.*, 1878, 86, 539, 1267; *Chem. Soc. Abs.*, 1878, 34, 586, 721.

[65] *Compt. rend.*, 1891, 113, 85; *Chem. Soc. Abs.*, 1891, 60, 1441.

[66] *Loc. cit.*

[67] British Patent 307,802, 1928; *Chem. Abs.*, 1930, 24, 127.

[68] British Patent 301,395, 1927; *Chem. Abs.*, 1929, 23, 4059. Hydrocarbon oils are cracked at 380° C. with boron fluoride at a pressure of 150 atmospheres.

[69] Bowlus and Nieuwland, *J.A.C.S.*, 1931, 53, 3835.

[70] Hinton and Nieuwland, *J.A.C.S.*, 1932, 54, 2017.

[71] Sowa, Hinton and Nieuwland, *J.A.C.S.*, 1932, 54, 2019.

[72] Hennion, Hinton and Nieuwland, *J.A.C.S.*, 1933, 55, 2857.

[73] Sowa, Hinton and Nieuwland, *J.A.C.S.*, 1932, 54, 3694.

[74] *Ber.*, 1933, 66, 411; *Chem. Abs.*, 1933, 27, 5053.

[75] The Friedel-Crafts reaction is discussed in Chapter 34 and various reactions of diolefins, in some of which boron fluoride is used, are discussed in Chapter 27.

[76] *Brennstoff-Chem.*, 1927, 8, 321; *Brit. Chem. Abs.* B, 1927, 930.

The polymerization of olefins, such as ethylene, propylene, and cyclohexene, with boron fluoride can also be accelerated by the presence of water, halogen acids, or halogen hydrocarbons capable of reacting with aromatic hydrocarbons in the Friedel-Crafts reaction, according to Hofmann, Otto and Stegemann.[78] For example, propylene was polymerized when treated with boron trifluoride and hydroiodic acid, ethyl fluoride or chloride. Butylene is produced in considerable proportions when liquid ethylene, together with a small quantity of boron trifluoride, is passed over a nickel catalyst at 150° C.[79] In most cases organic halogen compounds such as ethyl fluoride, and hydroxy-compounds, such as alcohols and water, have an accelerating effect on the reaction.

These polymerizations with boron fluoride can be utilized for many purposes. Pier and Christmann[80] treated fractions (obtained from a cracked paraffin oil and separated by treatment with solvents such as sulphur dioxide, aniline, or phenol) with boron fluoride, aluminum chloride, zinc chloride, or phosphorus oxychloride to obtain products usable as lubricating oils. The liquid fraction of a cracked paraffin wax, with an iodine value of at least 150 to 200, can be polymerized similarly.[81] Mineral oils have been refined by treatment with halides of boron, glucinum (beryllium), or bismuth,[82] or with gaseous or liquid hydrogen fluoride with or without the addition of metal halides.[83] Lubricating oils can also be produced by treating liquid olefins with liquid paraffin hydrocarbon mixtures, such as the product obtained by the hydrogenation of brown coal, in the presence of boron fluoride, aluminum chloride, or stannic chloride.[84] Gaseous olefins may be passed into the mixture during condensation.

Since boron fluoride is a gas which readily decomposes with moisture and is difficult to handle because of its corrosive and poisonous nature, double compounds with this substance, as has been previously mentioned, can be substituted for it in various reactions. Landolph[85] used the ethereal liquid condensate of ethylene and boron fluoride (ethylene fluoboric acid) with camphor. The previously mentioned boron trifluoride-acetic acid is another example. A double compound of ether and boron fluoride has been employed to condense saturated compounds with olefins[86] (see Chapter 24). Bruson[87] used an aryldiazonium fluoborate, phenyldiazonium fluoborate, $C_6H_5—N_2—BF_4$, for polymerizing indene, styrene, cyclopentadiene, coumarone, turpentine; also for treating rubber. When 20 per cent of phenyl tetrazonium difluoborate (obtained by diazotizing para-phenylenediamine, followed by coupling with fluoboric acid) was added to a highly unsaturated cracked gasoline (boiling range of 90° to 200° C.), which consisted of 45 per cent olefins, about 20 per cent of the reaction product boiling above 200° C. was a colorless oil containing a large proportion of resin. For raising the melting point of petroleum residues and soft paraffins Daitz[88] recommended treatment with ammonium or potassium bifluoride at a temperature below that of distillation.

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[77] French Patent 632,768, 1927; *Chem. Abs.*, 1928, **22**, 3417; British Patent 293,487, 1927; *Chem. Abs.*, 1929, **23**, 1648; U. S. Patent 1,811,130, June 23, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 4894; German Patents 505,265, 1926, and 512,959, 1927; *Chem. Abs.*, 1932, **26**, 479; German Patent 513,862, 1927; *Chem. Abs.*, 1933, **27**, 514.

[78] U. S. Patent 1,885,060, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 1006; British Patent 313,067, 1928; *Chem. Abs.*, 1930, **24**, 861; German Patents 504,730 and 507,919, 1933; *Chem. Abs.*, 1933, **27**, 4816. Hofmann and Stegemann, German Patent 524,891, 1928; *Chem. Abs.*, 1931, **25**, 4281; *cf.* Hofmann, *Chem.-Ztg.*, 1933, **57**, 5; *Brit. Chem. Abs.* **A**, 1933, 142.

[79] Otto and Bub, German Patent 545,397, 1928; *Chem. Abs.*, 1932, **26**, 2990; British Patent 326,322, 1929; *Brit. Chem. Abs.* **B**, 1930, 500; French Patent 682,055, 1929; *Chem. Abs.*, 1930, **24**, 4304; all patents assigned to I. G. Farbenindustrie A.-G.

[80] German Patent 546,082, 1930; *Chem. Abs.*, 1932. **26**, 3371.

[81] I. G. Farbenindustrie A.-G., British Patent 354,441, 1930; *Chem. Abs.*, 1932, **26**, 3915.

[82] Hofmann, Dunkel, Otto and Heyn, German Patent 550,429, 1926; *Chem. Abs.*, 1932, **26**, 4168.

[83] Hofmann and Stegemann, British Patents 292.932 and 292,933, 1927; *Chem. Abs.*, 1929, **23**, 1501.

[84] I. G. Farbenindustrie A.-G., British Patent 358.495, 1930; *Brit. Chem. Abs.* **B**, 1932, 10; see Chapter 24 for other examples of oils of this type.

[85] *Compt. rend.*, 1878, **86**, 1267.

[86] I. G. Farbenindustrie A.-G., French Patent 695.125, 1930; *Chem. Abs.*, 1931, **25**, 2435.

[87] U. S. Patent 1,892,101, Dec. 27, 1932; assigned to Resinous Products and Chemical Co.

PROPYLENE

Propylene is polymerized somewhat more readily than ethylene. Pyrolysis converts propylene into a complex mixture of liquid and gaseous hydrocarbons in which a hexene has not yet been identified. Possibly, under these conditions, the dimer, initially formed, undergoes rapid decomposition with the production of both saturated and unsaturated substances.

A considerable number of chemical substances exercise a strong polymerizing action on propylene. The pronounced tendency of propylene to polymerize to liquid hydrocarbons in the presence of concentrated sulphuric acid has been referred to previously. The polymerization of propylene in the presence of aluminum chloride[88a] and of boron trifluoride[89] is more rapid than that of ethylene and leads to the formation of a mixture of hydrocarbons, some of which are of high molecular weight. Michel[90] proposed to utilize the greater ease of polymerization of propylene and its homologues for the separation of ethylene from mixtures of these olefins. This is effected by passing the gas mixture through a suspension of aluminum chloride in an inert solvent (e.g., decalin) at atmospheric, or reduced pressure so that higher olefins are polymerized and the ethylene passes on substantially unchanged. Horsley[91] used cadmium phosphate for the same purpose, the ethylene being subsequently converted to ethyl alcohol.

The activity of floridin and other finely divided siliceous earths in polymerizing the amylenes was first noted by Gurwitsch.[92] Lebedev and Filonenko,[93] from a study of the polymerization of olefins by floridin at ordinary pressure, enunciated the generalization that only those olefin hydrocarbons are polymerized which are derivatives of the asymmetrical di- or tri-substituted ethylenes of the types $RR^1.C:CH_2$ and $RR^1C:CH.R^{11}$, while the mono-substituted or symmetrical di- and tetra-substituted olefins do not polymerize even over long periods in the presence of this material. In agreement with this generalization the above workers found that propylene was unaffected by floridin which, however, readily polymerized isobutylene. Later, however, Van Winkle[94] found that although propylene did not change in contact with activated floridin at atmospheric pressure, it did undergo condensation under increased pressures. After contact for two months, polymers were isolated which corresponded in boiling points with the dimer and trimer. At the end of one year's contact the products contained no dimer but only higher polymers (trimer, tetramer, and higher).

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[88] German Patent 572,446, 1928; *Chem. Abs.*, 1933, 27, 3069.

[88a] Szayna, *Przcmysl Chem.*, 1928, 12, 637; *Chem. Abs.*, 1929, 23, 1384.

[89] Butlerov and Gorianov, *Ann.*, 1873, 169, 147; *Ber.*, 1873, 6, 561; *Chem. Soc. Abs.*, 1873, 26, 873; Otto, *Brennstoff-Chem.*, 1927, 8, 321; *Brit. Chem. Abs.* B, 1927, 930; see section on boron fluoride.

[90] U. S. Patent 1,822,358, Sept. 8, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 5901.

[91] British Patent 374,510, 1932; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1932, 832.

[92] *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 827; *Chem. Abs.*, 1915, 9, 3005.

[93] *Ber.*, 1925, 58, 163.

[94] *J. Amer. Pharm. Assoc.*, 1928, 17, 544; *Chem. Abs.*, 1929, 23, 90.

Gayer[95] observed that the activity of floridin in polymerizing propylene at 350° C. can be increased by treatment with hydrochloric acid, which can be conveniently generated by the introduction of a small proportion of alkyl chloride. Traces of alkali or large quantities of water or oxygen poison the catalyst, but organic sulphur compounds do not impair its activity. Synthetic aluminum silicate has approximately the same activity as floridin but alumina adsorbed on a precipitated porous silica surface was about twenty times as active. Precipitated silica and synthetic ferric and magnesium silicates have no catalytic effect on the polymerization of propylene. The liquid polymer, obtained in 90 per cent yield from the crude product, is a colorless, practically gum-free volatile fuel having an octane number of 87. The fraction boiling up to 150° C. consists of olefin homologues from C_5 to C_9, inclusive (principally C_6).

The polymerization of propylene under the influence of the silent electric discharge was found by Prianischnikov[96] to produce a liquid product of density, 0.827; refractive index, n_D^{20} 1.4578; and mean molecular weight, 233; which consisted probably of the pentamer and higher polymers. The polymerization of propylene and cyclopropane with alpha-rays from radon (radium emanation) has been studied by Heisig.[97]

The polymerization of ethylene, propylene, and other olefins is said to be catalyzed by phosphoric acid or phosphorus pentoxide in the presence of a carrier such as active charcoal at temperatures below 400° C. and at increased pressure, to yield liquid products.[98]

It has been demonstrated by Lenher[99] that the presence of oxygen activates the thermal polymerization of propylene, and causes it to occur at much lower temperatures than in the absence of oxygen. By passing a mixture of propylene and oxygen (with the former in excess) through a fused-silica tube at 500° C. with a contact time of 7.8 seconds, 52 per cent of the propylene was polymerized to higher monolefins while the remainder (48 per cent) was oxidized to various oxygenated compounds. In the absence of oxygen, no polymerization could be detected under these conditions. The polymers formed at temperatures of 490° to 530° C. were found to consist entirely of higher monolefins, of which butylenes, amylenes and hexylenes were undoubtedly present. The oxygen-activated polymerization of propylene is therefore similar to that of ethylene (mentioned previously) in giving rise to a series of homologous monolefins. To explain this, Lenher advanced a mechanism which involves the activation of the double bond by the rupture of one of the carbon double bonds, and to the separation of free radicals by scission of the two carbon double bonds. The immediate homologues of propylene are thus considered to be formed by the reaction of the free methylene or ethylidene residues with propylene, yielding butylenes and amylenes, respectively.

BUTYLENES

Of the three isomeric butylenes, isobutylene is considerably more reactive than the others and especially so in its tendency to polymerize. The thermal treatment of isobutylene at temperatures of the order of 600° C. and at atmospheric pressure leads to the production of a complex mixture of liquid hydrocarbons of various types, in which it is difficult to distinguish the initial products of polymerization.[100] Under a pressure of 70 atmospheres at 380° to 400° C. isobutylene condenses to a mixture of higher paraffin, olefin, and cycloparaffin hydrocarbons, which resemble the products obtained by a similar treatment of ethylene, except that the fraction boiling below 150° C. is richer in olefins.[101] The olefins present were considered by Ipatiev to be a dimer and trimer of isobutylene. Evidence that the initial stage in the thermal polymerization of isobutylene is the production of higher olefins was presented by Lebedev and Koblianski,[102] who obtained what they considered to be triisobutylene (as well as higher polymers) by heating isobutylene at 200° C. in hard glass tubes for 14 days.

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[95] *Ind. Eng. Chem.*, 1933, 25, 1122.

[96] *Ber.*, 1928, 61, 1358.

[97] *J.A.C.S.*, 1932, 54, 2328.

[98] I. G. Farbenindustrie A.-G., British Patent 340,513, 1929; *Brit. Chem. Abs.* B, 1931, 333.

[99] *J.A.C.S.*, 1932, 54, 1830.

[100] Hurd and Spence, *J.A.C.S.*, 1929, 51, 3561.

Isobutylene polymerizes very readily in the presence of a large number of catalysts. The polymerization of this hydrocarbon by boron trifluoride at ordinary temperatures to yield high molecular weight oils has been described by Otto[103] and also by Butlerov and Gorianov.[104] The polymerization of a liquefied mixture of isobutylene and 2-butene at —10° C., in the presence of aluminum chloride or ferric chloride, is reported to yield a mixture of naphthenes.[105] The polymerization of isobutylene, as well as of other monolefins and diolefins, is effected with double complexes of aluminum chloride with nitrobenzene, nitromethane, acetone, benzophenone or diphenylsulphone and inorganic compounds such as silver chloride or cuprous chloride. Thus, 16.5 liters of isobutylene are passed at a gas rate of 4 liters per hour through a mixture of 10 grams of aluminum chloride, 10 grams of diphenylsulphone and 100 grams of benzene. As a result, 13.5 liters of the isobutylene are fixed with the production of a liquid consisting of 10 per cent diisobutylene, 15 per cent triisobutylene, and 65 per cent of higher polymers boiling above 200° C.[106]

The polymerization of isobutylene in the presence of activated floridin is of interest in that it exhibits a certain degree of reversibility. Lebedev and Koblianski[107] found that isobutylene polymerized readily in the presence of floridin (activated by heating to 300° C.) even at —80° C. At room temperature the polymerization was very rapid but it was retarded at temperatures of 200° C. and over. On passing the gas over the unheated catalyst, a marked evolution of heat (corresponding with the heat of polymerization) occurred. The products obtained by allowing liquid isobutylene to stand with floridin for 4 days at room temperature contained 4 per cent which boiled below 170° C., 25 per cent between 170° and 185° C., and 71 per cent above 185° C. However, by continuous passage of gaseous isobutylene over the catalyst, with removal of the polymers as formed, the product contained larger proportions of lower polymers, of which 18 per cent boiled below 170° C., 51 per cent between 170° and 185° C., and 31 per cent above 185° C. The liquid was further fractionated. Table 111 gives its composition.

The properties of the fractions in Table 111 were further investigated. The diisobutylene could be readily hydrogenated, proving its unsaturated nature, and polymerized to tetraisobutylene with floridin. The trimer, tetramer, and pentamer did not polymerize in the presence of the silicate and could be hydrogenated only slowly. From a mixture of di- and triisobutylene in the presence of floridin, pentaisobutylene appeared to be formed.

Lebedev and Koblianski[108] carried out a number of experiments on the

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[101] Ipatiev, *Ber.*, 1911, **44**, 2978.
[102] *Ber.*, 1930, **63**, 103; *J. Russ. Phys.-Chem. Soc.*, 1929, **61**, 2175; *Chem. Abs.*, 1930, **24**, 2423.
[103] *Brennstoff-Chem.*, 1927, **8**, 321; *Brit. Chem. Abs.* **B**, 1927, 930; see section on boron fluoride.
[104] *Ann.*, 1873, **169**, 147; *Ber.*, 1873, **6**, 561; *Chem. Soc. Abs.*, 1873, **26**, 873.
[105] Weizmann and Legg, British Patent 165,452, 1916; *J.S.C.I.*, 1921, **40**, 675A. U. S. Patent 1,395,620, Nov. 1, 1921.
[106] Bataafsche Petroleum Maatschappij, British Patent 358,068, 1931; *Brit. Chem. Abs.* **B**, 1932, 172.
[107] *Ber.*, 1930, **63**, 103.
[108] *Ber.*, 1930, **63**, 1432.

TABLE 111.—*Composition of Fractions from Polymerization of Isobutylene with Floridin.*

	Liquid Per Cent	B.P. ° C.	D^{20}_4
Diisobutylene	17	101–2°/762 mm.	0.7195
Triisobutylene	50	178.5–179.5/760 mm.	0.7600
Tetraisobutylene	17	106°/7 mm.	0.7944
Pentaisobutylene	5	148°/7 mm.	0.8176
Hexaisobutylene	1	158°–161°/2.5 mm.	0.8340
Heptaisobutylene	0.5	183°–186°/2 mm.	0.8455
Residue	9.5		

depolymerization of the higher polymers in the presence of this same catalyst. By passing these polymers over floridin at 200° C., the pentamer decomposed into a mixture of the trimer and dimer, the tetramer into two molecules of the dimer, the trimer into the dimer and isobutylene, and the dimer into two molecules of isobutylene itself. In all cases some monomeric isobutylene was produced, attributed in the cases of the tetramer and pentamer to progressive dissociation of the initial di- and tri-meric forms. Diisobutylene is the most stable polymer. The depolymerization of a mixture (average molecular weight of 840), obtained by distilling off the lower polymers up to and including the heptamer from the polymerized isobutylene, yielded a product containing more than 30 per cent of the trimer.

The polymerization of isobutylene in the presence of floridin has been investigated by Van Winkle[109] and also by Lebedev and Filonenko[110] with results similar to those already outlined. The generalization of the latter workers with regard to the greater tendency of unsymmetrical di- and tri-substituted ethylene to polymerize has already been discussed.[111]

Considerable work has been carried out on the polymerization of isobutylene by sulphuric acid of various concentrations. Comparatively dilute sulphuric acid (50 per cent) suffices to hydrate this olefin to tertiary butanol in the cold but stronger acid concentrations exert a profound polymerizing effect, especially at slightly elevated temperatures. Thus, Butlerov[112] found that, by warming a solution of isobutylene in 50 per cent sulphuric acid to 100° C., diisobutylene mainly is formed, while the introduction of isobutylene into acid of higher concentration (80 per cent and over) in the cold resulted in the formation of triisobutylene. Concentrated sulphuric acid converts isobutylene quantitatively into higher polymers.[113] Little is known of the constitutions of these polymers but they appear to be higher olefins and are far less reactive than isobutylene itself.

Whitmore and Wrenn[114] showed that the so-called "diisobutylene" (produced, for example, by decomposing 2500 grams of tertiary butanol with a mixture of 3300 cc. water and 2700 cc. of sulphuric acid) consists essentially of two isomeric octenes. Careful fractionation of the mixed dimer, which boiled at 100° to 105° C. at 738 mm., demonstrated the presence of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, the former being present in larger amount than the

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[100] *J. Amer. Pharm. Assoc.*, 1928, 17, 544; *Chem. Abs.*, 1929, 23, 90.

[110] *Ber.*, 1925, 58, 163.

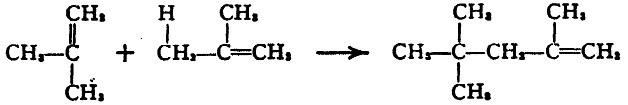
[111] Staudinger and Brunner (*Rubber Chem. and Tech.*, 1930, 3, 1375; *Chem. Abs.*, 1931, 25, 3519) investigated a mixture of very high molecular weight polymers obtained by the polymerization of isobutylene over floridin. This mixture, which was precipitated from ether solution by ethanol, was a viscous mass of d^{17}_4 0.9007, n^{17}_D 1.5022 and mean molecular weight 1600. It was stable to $KMnO_4$ and HNO_3, while Br_2 added to 50% of the theory for a polymer which contains 1 double bond to each 26 butylene units.

[112] *Ann.*, 1876, 180, 247; 1877, 189, 48; *Ber.*, 1879, 12, 1482.

[113] Nef, *Ann.*, 1901, 318, 26; *Chem. Soc. Abs.*, 1901, 80 (1), 626.

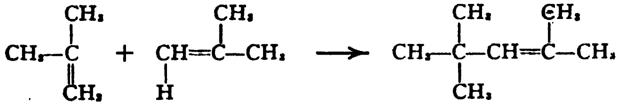
[114] *J.A.C.S.*, 1931, 53, 3136.

latter. Accordingly, the production of the mixed dimer from isobutylene may be represented graphically as follows:



$$CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_2\\ \|}}{C}} + \overset{\substack{H\\|}}{CH_2}-\overset{\substack{CH_3\\|}}{C}=CH_2 \longrightarrow CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-CH_2-\overset{\substack{CH_3\\|}}{C}=CH_2$$

2,4,4-trimethyl-1-pentene



$$CH_3-\underset{\substack{\|\\CH_2}}{\overset{\substack{CH_3\\|}}{C}} + \underset{\substack{|\\H}}{CH}=\overset{\substack{CH_3\\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-CH=\overset{\substack{CH_3\\|}}{C}-CH_3$$

2,4,4-trimethyl-2-pentene

The structure of these two isomeric diisobutylenes was proved by ozonation by McCubbin and Adkins[115] and later the compounds were isolated by Whitmore and his collaborators.[116]

The manufacture of polymerization products of isobutylene and of trimethylethylene has been accomplished by Müller-Cunradi and Eggert[117] by heating a solution of these gases absorbed in 50 to 60 per cent sulphuric acid for one-half hour at 100° C. Under these conditions the dimers, together with about 20 per cent of higher polymers, are said to separate from the acid. Polymers of iso-olefins, such as isobutylene, have been suggested as additions to lubricants, gasoline, and burning oils to improve their properties.[118]

Little work has been carried out on the polymerization of 1-butene and 2-butene, though it is definitely known that these olefins are more resistant to such changes than the isomeric isobutylene. Mailhe and Renaudie[119] heated 1- and 2-butene in the presence of silica gel at 650° to 700° C. and obtained liquid unsaturated hydrocarbons, benzene, toluene and m-xylene together with 40 per cent of propylene and 40 per cent of methane. In addition, 2-butene gave naphthalene and anthracene.

The condensation of 2-butene under the influence of the silent electric discharge was found by Prianischnikov[120] to yield an oil, having a mean molecular weight of 202, a density of 0.831, and an iodine number of 156, of which 30 per cent boiled below 150° C. The condensation of 2-butene to a dark viscous liquid under the influence of alpha-rays from radon (radium emanation) has been described by Heisig.[121]

AMYLENES

Although the polymerization of various amylenes under the influence of catalysts has been extensively investigated, the initial products of non-catalytic thermal polymerization have not been identified. Thermal treatment of the amylenes at temperatures of 500° C. and above at atmospheric pressure results in the production of both saturated and unsaturated hydrocarbons of higher and lower molecular weights than that of the parent amylene. Under pressure, however, condensation to liquid products occurs at much lower temperatures and consequently with less tendency for degradation of the initial products of reaction. By heating trimethylethylene in sealed glass tubes at 320° C. to 325° C., Engler and Routala[122] obtained complete conversion into products consisting largely of paraffinic and cycloparaffinic, with a relatively small amount of unsaturated hydrocarbons.

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[115] *J.A.C.S.*, 1930, 52, 2547; see Chapter 39 for discussion of this type of oxidation.

[116] Whitmore and Wrenn, *J.A.C.S.*, 1931, 53, 3136; Tongberg, Pickens, Fenske and Whitmore, *J.A.C.S.*, 1932, 54, 3706; Whitmore and Church, *J.A.C.S.*, 1932, 54, 3710.

[117] U. S. Patent 1,889,952, Dec. 6, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 1640. British Patent 322,102, 1928; *Brit. Chem. Abs.* B, 1930, 314.

[118] I. G. Farbenindustrie A.-G., French Patent 740,407, 1932; *Chem. Abs.*, 1933, 27, 2293.

[119] *Ann. combustibles liquides*, 1931, 6, 79; *Chem. Zentr.*, 1931, 2, 1270; *Brit. Chem. Abs.* A, 1932, 250.

[120] *Ber.*, 1928, 61, 1358.

[121] *J.A.C.S.*, 1931, 53, 3245.

The amylenes exhibit to a marked degree the power of isomerizing to a more stable form on heat treatment. For example, isopropylethylene is partially converted into trimethylethylene by passage over aluminum sulphate, phosphoric acid, or alumina at 420° to 500° C., though under the same conditions at 450° to 500° C. both trimethylethylene and 2-pentene are unchanged.[123] Similarly, Ipatiev[124] effected an 80 per cent conversion of isopropylethylene into trimethylethylene in the presence of silica at 500° to 505° C. or alumina at 525° to 535° C. At higher temperatures (670° C.) when passed over silica gel in a quartz tube, isoamylene yields 47 per cent lower olefins, 38 per cent methane, 7 per cent hydrogen and oil.[125] Under identical conditions 2-pentene decomposes to 52 per cent propylene and butylene, 34 per cent methane, 6 per cent hydrogen and an oil.

The greater stability of trimethylethylene and the ease of isomerization of the other amylenes into this substance account for the fact that it usually constitutes the preponderating constituent of the amylene fraction of cracked products. Bruylants[126] pointed out that the migration of a double bond usually occurs when the groups on each side of it possess markedly different residual affinities. In the synthesis of butenes, for example, 2-butene is formed almost exclusively. It appears to be a general rule that olefins of the $RCH_2CH:CH_2$ type (for example, 1-butene and isopropylethylene) are less stable than olefins of the $RCH:CHR$ type (exemplified by 2-butene and trimethylethylene) and tend to revert to the latter under the influence of heat, catalysts, and energy activations.[127] The shift of the double bond from the alpha to the beta position, as occurs in the isomerization of 1-butene to 2-butene and of isopropylethylene to trimethylethylene, also takes place with the higher olefins.[128] This is further exemplified by the ready conversion of 3,7-dimethyl-1-octene to 3,7-dimethyl-2-octene.

The condensation of "amylene" (in most cases consisting mainly of trimethylethylene), in the presence of anhydrous aluminum chloride has been studied by Aschan[129] and by Engler and Routala.[130] The products were similar to those obtained by the polymerization of ethylene under pressure in the presence of this reagent and consisted of saturated hydrocarbons of the paraffin and cycloparaffin series. At ordinary temperatures, condensation takes place in the presence of aluminum chloride with the formation of oils of high molecular weight.[131]

The polymerization of trimethylethylene in the presence of zinc chloride was found by Kondakov[132] to yield considerable proportions of diamylene. The very strong polymerizing action of floridin on "amylene" (mainly trimethylethylene) was also shown by Gurwitsch.[133] On mixing freshly distilled amylene with an equal weight of dried floridin at room temperature, polymerization took place with the evolution of heat, the product being principally the dimer. Polymerization of amylene was also brought about by carbon and by alumina and, with the latter, the heat development was even more pronounced than with floridin.

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[122] *Ber.*, 1909, 42, 4620.
[123] Norris and Reuter, *J.A.C.S.*, 1927, 49, 2624.
[124] *Ber.*, 1903, 36, 2003; *Bull. soc. chim.*, 1903, (3) 30, 115.
[125] Mailhe and Renaudie, *Compt. rend.*, 1931, 192, 561; *Chem. Abs.*, 1931, 25, 2682; see Chapter 2.
[126] *Bull. sci. acad. roy. Belg.*, 1924, 10, 492; *Chem. Abs.*, 1925, 19, 2322.
[127] Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., New York, 1929, 83.
[128] Zelinsky and Levina, *Ber.*, 1929, 62, 1861.
[129] *Ann.*, 1902, 324, 1; *Chem. Soc. Abs.*, 1902, 82 (1), 749.
[130] *Ber.*, 1909, 42, 4613.
[131] Engler and Routala, *Ber.*, 1910, 43, 388.
[132] *J. Russ. Phys.-Chem. Soc.*, 1893, 24, 309; *Chem. Soc. Abs.*, 1893, 64 (1), 382.

The polymerization and depolymerization of amylenes under the influence of floridin was studied by Lebedev and Vinogradov-Volzynski.[134] When heated with activated floridin, a mixture of trimethylethylene and methylethylethylene, yielded diamylene, which boiled at 37° to 39° C. This product when heated at 150° to 160° C. with the same catalyst decomposed into gaseous and liquid products, which consisted of methane and a mixture of butenes, isopropylethylene, isopentane, trimethylethylene, 3-methyl-2-pentene, heptene, octene, and nonene.

The polymerization of amylenes in the presence of sulphuric acid of various concentrations has been studied more thoroughly than that carried out in the presence of other agents. The production of "diamylene" by treatment of "amylene" (a mixture of isomers, but mainly trimethylethylene) with sulphuric acid (2 volumes concentrated acid to 1 volume of water) at room temperature was described by Butlerov,[135] Wischnegradsky,[136] von Schneider,[137] and other workers.[138] A comprehensive examination of this reaction was made later by Norris and Joubert.[139] The latter workers found that, of the amylenes, trimethylethylene and unsymmetrical methylethylethylene were polymerized most readily. In the case of these two most reactive isomers, polymerization could be effected with sulphuric acid of relatively low concentration, i.e., with 60 per cent sulphuric acid, at ordinary temperatures. Under these conditions, the products consisted mainly of the dimer. With more concentrated acid, polymerization was greatly accelerated and higher polymers were produced along with the dimer. Of the other three isomers, isopropylethylene was slowly polymerized by 70 to 75 per cent acid to form mainly the dimer, though with more concentrated acid, only higher polymers were formed. Both 1-pentene and 2-pentene were resistant to the polymerizing influence of acids of concentrations lower than about 80 per cent sulphuric acid. Concentrated acid converted these latter amylenes into polymers higher than the dimer. Norris and Joubert observed that relatively small quantities of acid are sufficient to effect this change. Thus, when 5 cc. of trimethylethylene were shaken with 0.65 cc. of concentrated sulphuric acid, polymerization occurred at once with the production of the dimer principally. Five cc. of this hydrocarbon were completely polymerized in 8 days by 0.4 cc. of sulphuric acid of 2:1 concentration. With 0.5 cc. of a more dilute (1:1) acid, about one-half of the hydrocarbon was converted. When 10 moles of isopropylethylene were shaken with 1 mole of concentrated sulphuric acid, a rise in temperature occurred and polymerization was complete in a few minutes, the product boiling above 200° C. Under similar conditions, trimethylethylene yielded mainly diamylene. When 10 moles of isopropylethylene were left in contact with 1 mole of 2:1 acid for 7 days, the product boiled at 153° to 158° C. and consisted almost entirely of the dimer.

The polymerized amylenes, as shown conclusively by Norris and Joubert, were olefins much more resistant to the action of chemical reagents than the parent substances. All the diamylenes decolorized a solution of bromine in carbon tetrachloride and reacted with ozone. The polymers were much more stable toward sulphuric acid than the monomeric amylenes and only reacted very slightly with hydrogen halides. It was found, however, that if the diamylene prepared either from trimethylethylene or isopropylethylene was shaken with sulphuric acid (3:1) for 2 days, a part of the hydrocarbon was converted into higher products, although solution in the acid did not appear to take place. This result explains why diamylenes are formed from amylene only with dilute acids. The action of various oxidizing agents on the diamylenes is of interest since it sheds some light on the constitution of these polymerized olefins. Oxidation with potassium permanganate or chromic acid was very slow but ozone readily combined with the diamylenes to form viscous ozonides. Decomposition of the ozonide of the diamylene from trimethylethylene with cold water yielded acetone, acetic acid, formic acid, and an acid of the formula $C_5H_{11}COOH$, as well as higher ketones. These results appear to indicate that the polymerization of trimethylethylene occurs according to the following[140]:

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[133] *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 827; *Chem. Soc. Abs.*, 1915, **108** (1), 933.

[134] *J. Russ. Phys.-Chem. Soc.*, 1928, **60**, 441; *Brit. Chem. Abs.* **A**, 1928, 732.

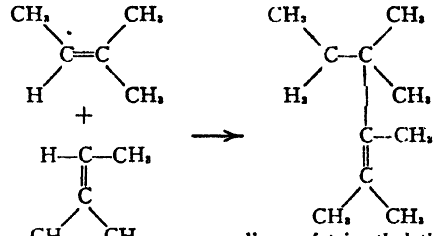
[135] *Ann.*, 1878, **189**, 44; *Chem. Soc. Abs.*, 1878, **34**, 121.

[136] *Ber.*, 1875, **8**, 434.

[137] *Ann.*, 1871, **157**, 185; *Chem. Soc. Abs.*, 1871, **24**, 216.

[138] Bauer, *Jahresber.*, 1861, 661; *Ann.*, 1865, **135**, 346; Berthelot, *Ann.*, 1863, **128**, 311; Erlenmeyer, *Z. für Chemie*, 1865, 365; Richter, *Ber.*, 1872, **5**, 334; *Chem. Soc. Abs.*, 1872, **25**, 1087; Lebedev, *Ber.*, 1875, **8**, 767; *Chem. Soc. Abs.*, 1876, **29**, 894.

[139] *J.A.C.S.*, 1927, **49**, 873.


dimer of trimethylethylene

As mentioned previously, trimethylethylene may be absorbed from gases in 50 to 60 per cent sulphuric acid, and if the solution is heated for one-half hour at 100° C., dimers, together with 20 per cent of other polymers, are formed.[141]

HIGHER OLEFINS

It has already been indicated that the higher dimeric olefins produced from the lower olefins are much more resistant to further polymerization, especially under the influence of sulphuric acid, than the parent olefin.

Thermal treatment of the higher olefins results in the formation of saturated and unsaturated hydrocarbons of both lower and higher molecular complexities (see Chapter 2). In the main, the most important changes involved in the pyrolysis of the higher olefins are rupture of the carbon chain with formation of radicals (probably accompanied by condensation), cyclicization, appearance of double bonds, and loss of hydrogen. Under pressure the polymerization of the higher olefins occurs at comparatively low temperatures and results, exactly as with the simpler members of the series, in the production of polymers and also of saturated hydrocarbons, probably of naphthenic structure. Thus, the condensation of 1-octene at 400° C. at a pressure of 500 kilograms per square centimeter (484 atmospheres) was observed by Hugel and Cohn[142] to furnish hydrocarbons liquid under those conditions. The same workers also found that the polymerization of hexadecene to a dimer and trimer was the only reaction observed when that hydrocarbon was heated to 300° C. at pressures varying from 5 to 1000 atmospheres. The polymerization was accelerated by increasing pressure and was considered to be an equilibrium. Other experiments [143] were carried out by heating hexadecene in tubes either completely or incompletely filled with the hydrocarbon. Distillation of the final products showed that when the olefin was present in the gas phase during the polymerization, a series of hydrocarbons boiling from 40° to 360° C. was obtained, whereas completely in the liquid phase only polymers of the original olefin were formed. The distillation curve in the latter case showed plateaux corresponding to $C_{16}H_{32}$, $C_{32}H_{64}$ and $C_{48}H_{96}$. These polymers of hexadecene were solid products similar to paraffin wax and apparently contained one double bond per molecule. Thermal treatment in the liquid phase under pressure appears to convert hexadecene into higher polymeric olefins. Hugel and Cohn [144] have isolated the dimeric hexadecene as a solid which melted at 53.8° to 54.8° C. and had an iodine value of 47 to 54. This substance was considered to be a straight-chain olefin with the ethylene bond located in the middle of the chain. It was found that, besides this solid dimer, liquid olefins of the formula $C_{32}H_{64}$ were simultaneously produced.[145] The latter substances were probably branched-chain olefins. The relative proportions of the solid and liquid dimers of hexadecene depended upon the experimental conditions, less of the solid polymer being formed under pressure at 400° C. than at 300° C.

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[140] *Cf.* Kondakov, *J. prakt. Chem.*, 1896, (2) **54**, 454; *Chem. Soc. Abs.*, 1897, **72** (1), 209. Brooks (private communication) isolated 5 different diamylenes made from trimethylethylene and determined the constitution of the dimer mentioned.

[141] I. G. Farbenindustrie A.-G., British Patent 322,102, 1928; *Brit. Chem. Abs.* **B**, 1930, 314.

[142] *Chimie et industrie* (Spec. No.), 1930, 201; *Chem. Abs.*, 1930, **24**, 5714; see also Hugel and Artichevitch, *Ann. combustibles liquides*, 1928, **3**, 985; *Chimie et industrie*, 1929, **21**, 953; *Chem. Abs.*, 1930, **24**, 1840. Hugel and Cohn, 9ème Cong. Chim. Ind., Barcelona, Oct. 1929; *J. Inst. Pet. Tech.*, 1929, **15**, 744.

The polymerization of the higher olefins by aluminum chloride or boron trifluoride has been little investigated. The work of Szayna [146] on the action of aluminum chloride on 1-octene and diamylene was carried out at such a temperature (100° to 150° C.) that the initial polymerization was obscured by the well-known splitting reactions induced by the aluminum chloride at those temperatures. To obtain polymerization products without fission products (such as lower paraffin hydrocarbons) it appears necessary to employ low temperatures and also, possibly, an inert liquid diluent. Quite recently Sullivan, Voorhees, Neeley and Shankland [147] produced lubricating oils by the action of about 2 per cent of aluminum chloride on olefins (pentenes, trimethylethylene, 1-hexene, 1-octene, and cetene) at 20° to 93° C. The conclusion reached by them was that the polymers produced in this way from the higher normal olefins possess a pronounced superiority over mineral lubricating oils, though this was not true of the polymers from the lower olefins such as ethylene.

Although the polymerizing action of sulphuric acid on higher olefins has been observed by Le Bel,[148] Rossolimo [149] and others, our knowledge of these reactions is due to a large extent to the work of Brooks and Humphrey.[150] These latter workers concluded that the polymerization of olefins under the influence of this reagent may be preceded by alcohol formation. Of the hexenes, tetramethylethylene appeared to be polymerized by sulphuric acid very readily. Thus, 46.5 grams of tetramethylethylene on treatment with 150 grams of 85 per cent sulphuric acid at 0° C. for 1 hour yielded 37.6 grams of a mixture of hydrocarbons in which the dimer predominated. On the other hand, 1-hexene on treatment with excess 85 per cent acid at 0° C. was hydrated to secondary hexanol, practically no polymers whatever being formed. The work of Brooks and Humphrey on the higher olefins is summarized in Table 112.

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[143] *Cf.* Hugel and Cohn, work discussed previously in this chapter (footnote 12).

[144] *Ann. combustibles liquides,* 1932, 7, 15; *Chem. Abs.,* 1932, 26, 4300.

[145] Hugel and Cohn, *Ann. combustibles liquides,* 1932, 7, 239; *Chem. Abs.,* 1932, 26, 5543.

[146] *Przemysl Chem.,* 1928, 12, 637; *Brit. Chem. Abs.* B, 1929, 117.

[147] *Ind. Eng. Chem.,* 1931, 23, 604.

[148] *Compt. rend.,* 1871, 73, 499; *Chem. Soc. Abs.,* 1871, 24, 1025; see Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 268.

[149] *J. Russ. Phys.-Chem. Soc.,* 1894, 1, 250; *Ber.,* 1894, 27, Ref. 626; the polymerization of octylene is discussed.

[150] *J.A.C.S.,* 1918, 40, 822.

TABLE 112.—*Polymerizing Effect of Sulphuric Acid on Olefins.*

Olefin	Acid Used Per Cent	Temp. ° C.	Products
3-Heptene	85	15	No polymers, only alcohol.
3-Methyl-2-pentene	95	0	Mainly alcohol, 10% dimer.
5-Methyl-1-hexene	85	—	Considerable proportion of dimer.
2-Octene	85	20	Mainly polymers.
5-Methyl-1-heptene	85	15	Mainly polymers, 50% dimer.
2-Methyl-2-undecene	85	20	Almost entirely dimer.
Hexadecene	85	20	Unaffected.
Hexadecene	95	—	Mixture of polymers.

It appears, therefore, that the action of sulphuric acid on the higher olefins results mainly or almost entirely in the formation of polymers, but as the molecular weight of the olefin increases so also does its resistance to the influence of sulphuric acid.[151] The straight-chain olefins are apparently more resistant to polymerization by this acid than are the highly branched-chain members, such as tetramethylethylene.

ACTION OF POLYMERIZING AGENTS ON CRACKED DISTILLATES

The cracking of petroleum usually gives products which contain considerable proportions of unsaturated hydrocarbons (see Chapter 3). Some methods of refining and purifying these cracked fractions, as has been previously mentioned, appear to be dependent on the polymerization of the olefin constituents, although little is known of the actual chemical mechanism.[152] A few of these processes are considered in so far as they relate to polymerization.

SULPHURIC ACID

The polymerization of individual olefins by sulphuric acid has been previously discussed.[153] Gerr and Tikhomirova[154] separated fractions of the polymerized oil which remained after passing a gas from cracked kerosene through cooled concentrated sulphuric acid. The original gas contained 33.6 per cent of relatively heavy hydrocarbons, 17.4 per cent of hydrogen, and 49 per cent of methane, but after passing through sulphuric acid the composition was 24 per cent heavy hydrocarbons, 20 per cent hydrogen, and 56 per cent methane. This decrease in the heavy hydrocarbon proportion was attributed to the polymerizing action of the sulphuric acid, which also gained 0.3 gram in weight for each liter of gas conducted through. An oil layer, corresponding to 0.0476 gram per liter of gas, was formed on the acid. This was separated into twelve fractions by distillation at a pressure of 2 millimeters. Odorless crystals which melted at 73° to 74° C. and had the empirical formula $C_{15}H_{24}$ were obtained from the fraction boiling at 99° to 130° C. at 2 mm. The fraction separated at 115° to 206° C. at this pressure was a viscous oil similar to lubricating oil. Similar results for a cracked light oil were reported by Bespolov.[155]

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[151] *Cf.* Michael and Brunel, *Amer. Chem. J.*, 1909, 41, 118; *Chem. Abs.*, 1909, 3, 1165.
[152] Tausz, *Z. angew. Chem.*, 1928, 41, 628.
[153] See, for example, Brooks and Humphrey, *loc. cit.*
[154] *Neft. Khoz.*, 1929, 16, 411; *Chem. Abs.*, 1929, 23, 4811.

An amylene fraction, which contained about 43 per cent of dissolved gases, from the vapor-phase cracking of crude oil, was treated with sulphuric acid at —45° C. by Marcovich and Pigulevski.[156] The product was fractionally distilled and saponified, from 12.8 to 25.5 per cent of the gas being converted into alcohols. They observed that 66 or 75 per cent acid dissolved more polymers than 85 per cent acid.

Ramage [157] treated hydrocarbon oils, which consisted essentially of olefin and aromatic hydrocarbons, with concentrated (66° Bé.) sulphuric acid. The oil was then fractionated. On nitration, the fraction which boiled below 100° C. yielded nitrobenzene, while that boiling between 100° and 120° C. produced nitrotoluene. The fraction obtained between 120° and 145° C. consisted of xylenes and olefins, that between 145° and 300° C. of olefins up to pentadecene, and that between 300° and 450° C. resembled a lubricating oil.

In a process of refining petroleum products or of making gasoline proposed by Brooks,[158] cracked petroleum rich in olefins is subjected to the action of sulphuric acid (specific gravity less than 66° Bé.), after which the oil is separated, treated with an alkali and distilled. Diolefins are resinified, but monolefins are practically unaffected by this treatment. Polymers formed in the refining with sulphuric acid can be removed by distillation over silica gel, charcoal or similar adsorbents.[159] Demant [160] treated solvent naphtha with sulphuric acid to obtain a viscous oil with a freezing point of —10° to —15° C.

ALUMINUM HALIDES

By heating unsaturated hydrocarbons such as ethylene or propylene to 260° to 540° C. under pressures of 40 to 120 kilograms per square centimeter (40 to 120 atmospheres) in the presence of aluminum chloride or bromide, polymerization results.[161] Unsaturated hydrocarbons of high molecular weight can be prepared by directing olefins of low molecular weight at a temperature below 300° C. over vaporizable halogenated compounds such as aluminum chloride, with a time of contact less than 100 seconds.[162]

A number of processes in which synthetic lubricating oils are prepared by polymerization in the presence of aluminum chloride have been proposed (see also Chapter 5). In one such method, solid or semi-solid aliphatic hydrocarbons having a mean molecular weight of not less than 170 (paraffin wax) are polymerized with agents capable of introducing exchangeable substituents such as chlorine, oxygen, and sulphur, in the presence of catalysts such as aluminum chloride.[163] Cyclic or olefin hydrocarbons also may be present. Unsaturated hydrocarbons which result from the cracking of hydrocarbon materials containing a high proportion of normal paraffin hydrocarbons can also be polymerized with aluminum chloride to yield lubricating oils.[164] A double compound of aluminum chloride and ethylene, made by passing ethylene at 40° to 60° C. through a suspension of aluminum chloride in a saturated hydrocarbon, will also effect polymerization, according to Häuber.[165]

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[155] *Neft. Khoz.*, 1929, **16**, 730; *Chem. Abs.*, 1930, **24**, 1731.

[156] *Neft. Khoz.*, 1930, **18**, 627; *Brit. Chem. Abs.* **A**, 1931, 283.

[157] U. S. Patent 1,483,835, Feb. 12, 1924; assigned to Bostaph Engineering Corp.; *Chem. Abs.*, 1924, **18**, 1194.

[158] U. S. Patent 1,563,012, Nov. 24, 1925; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1926, **20**, 501.

[159] Miller and Connolly, British Patent 373,174, 1932; *Chem. Abs.*, 1933, **27**, 4068; French Patent 710,094, 1931; *Chem. Abs.*, 1932, **26**, 1111; both patents assigned to Silica Gel Corp.

[160] British Patent 179,610, 1921; *J.S.C.I.*, 1922, **41**, 539A.

[161] Pure Oil Co., French Patent 680,038, 1929; *Chem. Abs.*, 1930, **24**, 3799.

[162] Pungs and Rabe, U. S. Patent 1,923,583, Aug. 22, 1933; *Chem. Abs.*, 1933, **27**, 5181; French Patent 718,346, 1931; *Chem. Abs.*, 1932, **26**, 2986; French Patent 717,056, 1931; *Chem. Abs.*, 1932, **26**, 2747; all patents assigned to I. G. Farbenindustrie A.-G.

[163] I. G. Farbenindustrie A.-G., British Patent 349,071, 1930; *Brit. Chem. Abs.* **B**, 1931, 832.

To manufacture lubricating oil, Howes [166] polymerized olefins at 15° C. at a pressure of 70 atmospheres in the presence of a catalyst which consists of Florida earth impregnated with finely divided nickel and anhydrous aluminum chloride.

A solid absorptive catalyst capable of polymerizing unstable hydrocarbons, such as Florida earth, has been used by Gray [167] to refine hydrocarbon vapors from which sulphur compounds have been removed previously by basic mercuric acetate. Fuller's earth and similar adsorptive materials,[168] aluminum chloride [168a] and sodium metal [168b] have been used to remove gum-forming and color-imparting substances from cracked distillates. Kalichevsky and Ramsay [168c] studied the factors which influence the refining of lubricating oils with adsorbent clays. Considerable paraffin is lost in the refining with fuller's earth. According to Fussteig [168d] adsorbed paraffin can be recovered by extraction of the spent earth with light gas oil at 90° C. The refining of cracked distillates by subjecting them to the action of liquid sulphur dioxide containing metallic halides (mercuric, stannic, or titanium chlorides) soluble therein was described by Davis.[168e]

POLYMERIZATION BY HEAT

The polymerization of individual olefins by heat has been discussed in other chapters (see Chapters 2 and 4) as well as in this. As previously stated, Dunstan, Hague and Wheeler [168f] observed that below about 550° C., at 150 pounds per square inch pressure, polymerization occurs and that by controlling the temperature, pressure, contact surface, and time of contact, the products may be varied from gaseous liquid hydrocarbons to viscous oils having lubricating qualities.

By distillation of an oil in the presence of an absorbing agent such as fuller's earth, bentonite, or charcoal, Morrell [169] obtained a resinous material which could be removed from the absorbent with alcohol and ether, liquid sulphur dioxide, or other solvents. In one process, liquid hydrocarbons were obtained from olefins by heating them at about 350° to 800° C. under a pressure of about 1000 atmospheres in contact with metals such as tin, zinc, aluminum, chromium, silicon, lead, or their alloys.[170] Catalysts such as aluminum chloride may also be present.

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[164] Standard Oil Co. of Indiana, French Patent 690,966, 1930; *Chem. Abs.*, 1931, **25**, 1376.

[165] German Patent 557,305, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 304. British Patent 345,334, 1929; *Chem. Abs.*, 1932, **26**, 155.

[166] British Patent 372,763, 1932; assigned to Imperial Chemical Industries, Ltd., *Chem. Abs.*, 1933, **27**, 3599. U. S. Patent 1,877,664, Sept. 13, 1932; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, **27**, 187.

[167] U. S. Patent 1,825,861, Oct. 6, 1931; assigned to Gray Processes Corp.; *Brit. Chem. Abs.* **B**, 1932, 714; Gray and Mandelbaum, *Ind. Eng. Chem.*, 1924, **16**, 913.

[168] Gray, U. S. Patent 1,901,158, Mar. 14, 1933; *Chem. Abs.*, 1933, **27**, 3068; U. S. Patent 1,865,467, July 5, 1932; *Brit. Chem. Abs.* **B**, 1933, 537; U. S. Patent 1,340,889, May 25, 1920; *J.S.C.I.*, 1920, **39**, 651A; U. S. Patent 1,908,599, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3811; all patents assigned to Gray Processes Corp.; Watson, U. S. Patent 1,894,331, Jan. 17, 1933; assigned to Pure Oil Co.; *Chem. Abs.*, 1933, **27**, 2571; Stormonth, U. S. Patent 1,903,370, April 4, 1933; *Chem. Abs.*, 1933, **27**, 3326; Osterstrom, U. S. Patent 1,891,109, Dec. 13, 1932; assigned to Pure Oil Co.; *Chem. Abs.*, 1933, **27**, 2026; Darrow and Sweeney, U. S. Patent 1,903,094, Mar. 28, 1933; *Chem. Abs.*, 1933, **27**, 3323; Morrell, U. S. Patent 1,904,381, April 18, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 3600.

[168a] I. G. Farbenindustrie A.-G., French Patent 679,225, 1929; *Chem. Abs.*, 1930, **24**, 3897; see also Chapter 5.

[168b] Cross, U. S. Patents 1,859,027 and 1,859,028, May 17, 1932; assigned to Cross Development Corp.; *Brit. Chem. Abs.* **B**, 1933, 295; Carlisle and Harris, U. S. Patent 1,862,003, June 7, 1932; assigned to Roessler and Hasslacher Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 537.

[168c] *Ind. Eng. Chem.*, 1933, **25**, 941.

[168d] *Petroleum Z.*, 1930, **26**, 627; *Chem. Abs.*, 1930, **24**, 4621.

[168e] U. S. Patent 1,941,251, Dec. 26, 1933; assigned to Universal Oil Products Co.

[168f] *J.S.C.I.*, 1932, **51**, 131T.

[169] U. S. Patent 1,608,135, Nov. 23, 1926; *Chem. Abs.*, 1927, **21**, 318. Resinous oxygen-absorbing olefin polymers have also been recovered from cracked distillates by Morrell (U. S. Patent 1,888,044, Nov. 15, 1932; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 1530) and by Hyman (U. S. Patents 1,919,722 and 1,919,723, July 25, 1933; assigned to Versicol Corporation; *Chem. Abs.*, 1933, **27**, 4942).

Ethylene and its homologues, for example, cracked petroleum products or destructive hydrogenation products with olefin properties, can be polymerized to products boiling between 100° and 200° C. by heating them to 420° C. under a pressure of 45 atmospheres without catalysts in the presence of an inert liquid such as mineral or vegetable oil.[171] Wagner[171a] polymerized cracked gaseous distillates to gasoline-like products by heating to between 175° and 375° C. under a pressure above 40 atmospheres in the presence of metals of Group VIII of the periodic system (platinum or palladium).

Electric Discharges

In a previous chapter (Chapter 9) the action of electric discharges on hydrocarbons was discussed. Feiler[172] prepared diolefins from ethylene and other lower olefins by exposing the gases at a high rate of flow to the action of high-temperature electric discharges. The process is carried out in a closed cycle with continuous removal of higher olefins by cooling.

Polymerization products have also been obtained from gases which contain methane, ethylene, acetylene, and their homologues by subjecting them to the action of electrical fields such as high-frequency oscillations at high temperatures (above 900° C.).[173]

Polymerization of Styrene and Other Aryl-Substituted Olefins

The marked influence of the introduction of electronegative groups on the tendency of polymerization of unsaturated hydrocarbons is exemplified by styrene. The polymerization reactions of the aryl-substituted olefins, and particularly of styrene,[174] $C_6H_5.CH{=}CH_2$, are of interest both because of the relative ease of polymerization and the resinous character of many of the polymers produced. The arylalkenes exhibit a behavior similar to that of the simpler conjugated diolefin hydrocarbons. Polystyrene,[175] which is the product of polymerization of styrene either by heat, catalysts or under the influence of light, is a transparent vitreous substance of high molecular weight, insoluble in water, alcohol and petroleum hydrocarbons, but soluble in benzenoid hydrocarbons, chlorinated hydrocarbons and in esters. The physical properties of polystyrene are such as to render it a valuable synthetic plastic and, with the development of methods of producing styrene (e.g., by pyrolysis of ethylbenzene, formed by condensation of ethylene and benzene[176]) there can be no doubt that polystyrene will become of great technical importance.[177]

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[170] I. G. Farbenindustrie A.-G., British Patent 309,199, 1927; *Chem. Abs.*, 1930, 24, 377; British Patent 316,422, 1928; *Brit. Chem. Abs.* **B**, 1929, 804; French Patent 666,611, 1929; *Chem. Abs.*, 1930, 24, 1389; British Patent 336,234, 1929; *Chem. Abs.*, 1931, 25, 1839. *Cf.* British Patent 313,123, 1929; *Brit. Chem. Abs.* **B**, 1931, 54.

[171] Bataafsche Petroleum Maatschappij, French Patent 690,935, 1930; *Chem. Abs.*, 1931, 25, 1259; British Patent 331,186, 1929; *Chem. Abs.*, 1931, 25, 114. See also French Patent 743,789, 1933; *Chem. Abs.*, 1933, 27, 4072; German Patent 573,532, 1933; *Chem. Abs.*, 1933, 27, 4244.

[171a] U. S. Patent 1,913,691, June 13, 1933; assigned to Pure Oil Co.; *Chem. Abs.*, 1933, 27, 4390.

[172] U. S. Patent 1,799,787, April 7, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 3012.

[173] Ruhrchemie A.-G.; British Patent 355,210, 1929; *Chem. Abs.*, 1932, 26, 4065.

[174] Other names for this compound are styrol, styrolene, vinylbenzene, phenylethylene and cinnamene.

[175] This polymer has been referred to as "metastyrene" in the past. It appears advisable to replace the prefix "meta," which is used to denote a position of substitution in the benzene ring, by the prefix "poly," as suggested by Staudinger, "Die hochmolekularen organischen Verbindungen," Springer, Berlin, 1932.

The thermal polymerization of styrene proceeds rapidly (½ hour) in a sealed tube at 200° C. and more slowly (3 days) at 100° C.[178] At ordinary temperatures the polymerization of styrene proceeds extremely slowly in the dark,[179] although as demonstrated later, exposure to air results in the production of oxidized material which has a pronounced catalytic action on the speed of polymerization. The polymerization of styrene is accelerated by exposure to light. Exposure of styrene to sunlight at room temperature brought about the production of polystyrene in 3 weeks.[180] The photopolymerization of styrene is said to be incomplete and to lead to an equilibrium, $x\,C_8H_8 \rightleftarrows (C_8H_8)_x$. The partial reconversion of polystyrene to styrene takes place under the influence of sunlight and also by distillation.[181]

The polymerization of styrene (to polystyrene) is accelerated by catalysts, such as sulphuric acid.[182] According to Brooks and Humphrey,[183] 85 per cent sulphuric acid at 0° C. converts styrene into a hard resin. Polystyrene is produced by heating styrene with an aqueous solution of sodium bisulphite at 100° to 120° C.[184]

It has long been known that the presence of air or oxygen increases the tendency of styrene to polymerize.[185] Thus, Stobbe and Posnjak[186] found that styrene which had stood for 14 days was polymerized much more rapidly by heat and light than the freshly distilled hydrocarbon. Houtz and Adkins[187] also showed that the polymerization of styrene was accelerated by the presence of up to 2 per cent of ozonized diisobutylene. Though a polymerized styrene peroxide is simultaneously produced during the oxygen-activated polymerization of liquid styrene, it is doubtful whether this peroxide is the actual catalyst. Staudinger and Lautenschläger[188] have adduced evidence in support of the view that the peroxide is not the actual catalyst but that a primary oxide, formed during autoxidation, is the principal agent.

A number of other catalysts, such as anhydrous metallic halides, aryldiazonium fluoborates[189] and others,[190] promote the polymerization of styrene. Krakau[191] observed that the rate of polymerization of styrene is reduced by the presence of small amounts of elemental bromine, iodine, or sulphur. Pummerer and Kehlen[192] exposed styrene to visible or ultraviolet rays in the presence of a small amount of an aldehyde or ketone to effect polymerization.

Besides polystyrene, a liquid dimer (distyrene) has also been obtained by heating styrene to 170° C. with concentrated hydrochloric acid, or by the action of a mixture of concentrated sulphuric and glacial acetic acids on styrene.[193] Distyrene, which is not depolymerized to styrene by heating, is identical with 1,3-diphenyl-1-butene which has the constitution:

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[176] e.g., Mark and Wulff, German Patent 550,055, 1929; *Chem. Abs.*, 1932, **26**, 4069; British Patent 340,587, 1929; *Brit. Chem. Abs.* **B**, 1931, 335; French Patent 702,377, 1930; *Chem. Abs.*, 1931, **25**, 4285; see Chapter 4 for other methods of preparing styrene.

[177] See Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York.

[178] Blyth and Hofmann, *Ann.*, 1845, **53**, 291, 311. *Cf.* Ostromislensky, U. S. Patent 1,683,402, Sept. 4, 1928; British Patent 236,891, 1925; *Chem. Abs.*, 1926, **20**, 1243.

[179] Lemoine, *Compt. rend.*, 1897, **125**, 530; *Chem. Soc. Abs.*, 1898, **74** (1), 70.

[180] Lemoine, *Compt. rend.*, 1899, **129**, 719; *Chem. Soc. Abs.*, 1900, **78** (1), 91.

[181] Thus, Kronstein (*Ber.*, 1903, **35**, 4150, 4154) obtained a 60% yield of styrene and a residue soluble in benzene by distillation of polystyrene.

[182] Berthelot (*Bull. soc. chim.*, 1866, (2) **6**, 296) appears to have been the first to study the action of sulphuric acid on styrene.

[183] *J.A.C.S.*, 1918, **40**, 825.

[184] Miller, *Ann.*, 1877, **189**, 361; *cf. Ber.*, 1876, **9**, 1450; *Chem. Soc. Abs.*, 1878, **34**, 885.

[185] *Cf.* Simon, *Ann.*, 1839, **31**, 267; see Gmelin, "Handbook of Chemistry" (translated by Watts), Cavendish Society, London, 1859, **13**, 1.

[186] *Ann.*, 1909, **371**, 259; *Chem. Abs.*, 1910, **4**, 2120. Stobbe, *Ann.*, 1915, **409**, 1; *Chem. Abs.*, 1915, **9**, 1755.

[187] *J.A.C.S.*, 1931, **53**, 1058; *ibid.*, 1933, **55**, 1609. *Cf.* Staudinger and Heuer, *Ber.*, 1930, **63B**, 222.

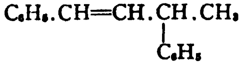
[188] *Ann.*, 1931, **488**, 1; *Brit. Chem. Abs.* **A**, 1931, 1031.

[189] Bruson, U. S. Patent 1,892,101, Dec. 27, 1932; assigned to Resinous Products and Chemical Co.

[190] See, e.g., Schlenk, Appenrodt, Michael and Thal (*Ber.*, 1914, **47**, 476) on the use of metallic sodium and potassium.

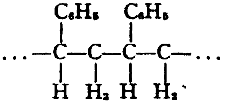
[191] *J. Russ. Phys.-Chem. Soc.*, 1878, **10**, 238; *Ber.*, 1878, **11**, 1259.

[192] German Patent 576,141, 1933; *Chem. Abs.*, 1933, **27**, 3721.



$$C_6H_5.CH{=}CH.\underset{\displaystyle C_6H_5}{\underset{|}{CH}}.CH_3$$

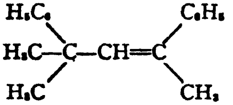
Staudinger[194] represents polystyrene as a long chain of styrene groups formed by end to end combination at the olefin double bond, as follows:



$$\ldots-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}-\underset{\displaystyle H_2}{\underset{|}{C}}-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}-\underset{\displaystyle H_2}{\underset{|}{C}}-\ldots$$

It is therefore a long methylene-chain substituted alternately by phenyl groups. The number of these styrene units in the more highly polymerized forms has been estimated at several thousand.

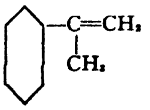
Of the homologues of styrene, *a-methylstyrene* (formula 1 below) is not readily polymerized by light or heat but is converted by the action of sulphuric acid into a crystalline dimer[195] which probably has the formula:



This dimer can be partly depolymerized to the parent hydrocarbon by heating. In a similar way, *β-methylstyrene* (formula 2) is polymerized by light or by catalysts, such as ferric chloride, to a crystalline saturated dimer.[196]

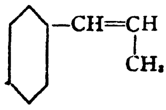
Of the other aryl-substituted ethylenes, *1,1-diphenylethylene*[197] (formula 3) is remarkably stable, whereas *1,1-diphenyleneethylene* (formula 4) is readily converted to a high molecular weight polymer even in diffused daylight.[198]

(1)



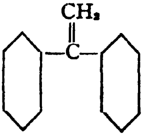
a-methylstyrene

(2)



β-methylstyrene

(3)



1,1-diphenylethylene

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[193] Stobbe and Posnjak, *Ann.*, 1909, **371**, 287; *cf.* Erlenmeyer, *Ann.*, 1910, **372**, 247; *Chem. Abs.*, 1910, **4**, 2129; Stobbe, *Ann.*, 1910, **372**, 249; *Chem. Abs*, 1910, **4**, 2129.

[194] Staudinger, "Die hochmolekularen organischen Verbindungen," Springer, Berlin, 1932. See also Ellis, *Ind. Eng. Chem.*, 1933, **25**, 125.

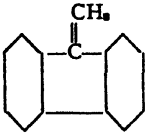
[195] Perkin, *J.C.S.*, 1877, **32**, 660; Klages, *Ber.*, 1902, **35**, 2640; Tiffeneau, *Ann. chim. phys.*, 1907, (8) **10**, 157; *Chem. Abs.*, 1907, **1**, 3005. For a discussion of this formula see Bergmann, Taubadel and Weiss, *Ber.*, 1931, **64**, 1493; *Chem. Abs.*, 1931, **25**, 4239; Staudinger and Breusch, *Ber.*, 1929, **62**, 442.

[196] Errera, *Gazz. chim. ital.*, 1885, **14**, 504; *Chem. Soc. Abs.*, 1885, **48**, 772. Angeli and Mole, *Gazz. chim. ital.*, 1894, **24** (2), 128; *Chem. Soc. Abs.*, 1895, **68** (1), 24; Ciamician and Silber, *Ber.*, 1909, **42**, 1389; Dafert, *Monatsh.*, 1883, **4**, 623; *Chem. Soc. Abs.*, 1883, **44**, 1093.

[197] Hildebrand, Diss. Strassbourg, 1909; Lebedev, Andreevski and Matiuschkina, *Ber.*, 1923, **56**, 2349.

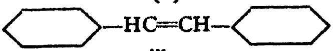
[198] Wieland, Reindel and Ferrer, *Ber.*, 1922, **55**, 3313; Ferrer, *Anal. soc. espan. fin. quim.*, 1922, **20**, 459; *Chem. Abs.*, 1923, **17**, 3177.

(4)



1,1-diphenyleneethylene

(5)



stilbene

Stilbene (sym.-diphenylethylene) (formula 5 above) is polymerized in benzene solution under the influence of sunlight to yield a dimer which is tetraphenylcyclobutane.[199] This photopolymerization is said to be reversible, the position of the equilibrium $2C_{14}H_{12} \rightleftharpoons C_{28}H_{24}$ depending upon the wave length of the light.

The polymerization products of styrene find application as plastic materials, for example, in the manufacture of cast, molded and lathe-turned articles and as coating materials. They have also been added to lubricating oils to improve their properties and increase their viscosity.[200] Hydrogenated polystyrene or hydrogenated polymerized diolefins can also be used for this purpose. Instead of adding polymerized styrene as such to the oil directly, styrene itself may be added, it then being polymerized and hydrogenated in the oil.

UTILIZATION OF OLEFIN POLYMERS

Large quantities of dimers of the simple monolefins are undoubtedly produced during the refining of cracked gasolines with sulphuric acid. Besides the uses already mentioned, these dimers appear to be quite valuable constituents of motor spirit since Howes and Nash[201] found that diisobutylene and the diamylenes (especially the diamylene prepared from trimethylethylene) possess excellent antidetonating properties.[202] The conversion of olefins to high molecular weight oils capable of being utilized as lubricants, by polymerization under the influence of aluminum chloride or boron trifluoride, is an interesting development in the application of the olefins. An account of industrial developments in the production of lubricants from gaseous and liquid olefins by this method has been presented by Sullivan and Voorhees and their collaborators.[203]

The production of a mixture of liquid paraffins and unsaturated drying oils for use in varnishes by polymerization of gaseous unsaturated hydrocarbons with sulphuric or phosphoric acid, has been effected.[204] A residue obtained by Zilberman, Bolotin and Yakubovich[204a] from the residues of oil cracking, consisting of fractions boiling between 185° and 243° C., was found to reduce the oil-absorption capacity of pigments and could be substituted to the extent of about 75 per cent for linseed oil. This polymerized material had a specific gravity of 0.858, iodine number of 80.7, acid number of 1.9, and saponification number of 28.66.

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[199] Ciamician and Silber, *Ber.*, 1902, **35**, 4129; Stobbe, *Ber.*, 1914, **47**, 2703; *Z. angew. Chem.*, 1922, **35**, 578.

[200] Wulff, Moll and Breuers, German Patent 557,306, 1930; *Chem. Abs.*, 1933, **27**, 410; also British Patent 379,717, 1931; *Brit. Chem. Abs.* **B**, 1932, 971; Pungs and Frese, German Patent 567,350, 1928; *Chem. Abs.*, 1933, **27**, 1502; German Patent 574,753, 1933; *Chem. Abs.*, 1933, **27**, 4666; all patents assigned to I. G. Farbenindustrie A.-G.

[201] *J.S.C.I.*, 1930, **49**, 113T. Production of motor fuels by polymerization of olefins is described by Wagner, British Patent 341,391, 1929; *Chem. Abs.*, 1931, **25**, 5007; Texaco Development Corp., French Patent 739,846, 1932; *Chem. Abs.*, 1933, **27**, 2294; Reid, U. S. Patent 1,912,009, May 30, 1933; assigned to Columbia Engineering and Management Corp.; *Chem. Abs.*, 1933, **27**, 4058; Standard Oil Co. of Indiana, French Patent 746,265, 1933; *Chem. Abs.*, 1933, **27**, 4654.

[202] *Cf.* I. G. Farbenindustrie A.-G., French Patent 740,407, 1932; *Chem. Abs.*, 1933, **27**, 2293. Polymerized gaseous olefins as sources of liquid fuels are discussed by Bowen and Nash (*World Petroleum Congress*, July 19-25, 1933; Preprint No. 79).

[203] Sullivan, Voorhees, Neeley and Shankland, *Ind. Eng. Chem.*, 1931, **23**, 604; Sullivan, Voorhees, Oak and Barnard, *J. Soc. Automotive Engrs.*, 1931, **29**, 40; *Chem. Abs.*, 1932, **26**, 5409. Production of oils by polymerization of olefins is described by I. G. Farbenindustrie A.-G., French Patent 709,734, 1931; *Chem. Abs.*, 1932, **26**, 1435; Pungs and Hartmann, German Patent 544,292, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2471; Bataafsche Petroleum Maatschappij, French Patent 747,500, 1933; *Chem. Abs.*, 1933, **27**, 5183; Howes, British Patent 372,763, 1932; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1933, **27**, 3599; Pyhälä, *Mat. grasses Pétr. Dériv.*, 1932, **23**, 9312, 9340; *ibid.*, 1932, **24**, 9452; *Chem. Zentr.*, 1933, **1**, 877; *Brit. Chem. Abs.* **B**, 1933, 819.

[204] New Oil Refining Process Ltd., British Patent 10,040, 1913; *Chem. Abs.*, 1914, **8**, 3500.

[204a] *Lakokrasochnuyu Ind.*, 1933, No. 1, 37; *Chem. Abs.*, 1933, **27**, 4695.

The liquid polymerization products of olefins may be used as solvents for organic substances such as ethylcellulose, rubber, fats, waxes, and bitumens.[205] For the preparation of varnishes and paints, Chittick[205a] heated for 1 hour at 150° to 260° C., 4 parts by weight of a drying or semi-drying oil (linseed or tung oil) with 6 parts of reduced hydrocarbon polymers obtained by catalytic action of unsaturated residues from petroleum at high temperatures. The mixture was subsequently cooled to 95° C. and 1 part of japan drier and 0.5 part of turpentine or naphtha were added. Robinson[205b] used polymers resulting from washing oil gas with sulphuric acid for the denaturing of alcohol.

The numerous methods for the production of liquid hydrocarbons by the thermal treatment of gaseous or low-boiling olefins are discussed elsewhere (see Chapters 2, 5 and 6).

POLYMERIZATION OF DIOLEFINS

Unsaturated hydrocarbons with two ethylene linkages in the molecule exhibit a great tendency to polymerize under the influence of many comparatively mild reagents. This is particularly true in the case of conjugated dienes like butadiene,

$$CH_2{=}CH{-}CH{=}CH_2$$

and its derivatives, which polymerize readily to high molecular weight, amorphous, rubber-like substances. In polymerizing diolefins, comparatively mild conditions must be employed, since the use of reagents which are successful in polymerizing monolefins, such as aluminum chloride and sulphuric acid, leads to the formation of tars and resins of less value.[206]

Two main types of polymerization may be clearly distinguished in the diolefin series, namely,[207] (1) the allene type in which hydrocarbons of the type $>C{=}C{=}C<$ yield cyclobutane derivatives, and (2) the 1,3-butadiene or isoprene type, which tend to furnish unsaturated cyclohexane hydrocarbons, as well as amorphous polymers of high molecular weight, some of which are rubber-like masses.

ALLENES

When heated in the liquid state at 140° C. under pressure for 3½ days, allene (propadiene, $CH_2{=}C{=}CH_2$) is converted to the extent of about 50 per cent into a mixture of polymers consisting of 5 per cent dimer, 15 per cent trimer, 5 per cent α-tetramer, 22 per cent β-tetramer, 18 per cent pentamer, 10 per cent hexamer, and 25 per cent of a colorless gum-like solid.[208] When pyrolyzed at higher temperatures at atmospheric pressure both allene and methylallene yield large quantities of liquid polymers. A temperature of about 500° C. was found most appropriate for the formation of liquids from allene by pyrolysis in a pyrex tube. Above that temperature considerable cracking occurred with the formation of liquid products.[209] With methylallene, complete decomposition was effected at 500° to 550° C. in 36 seconds and 75 per cent of the hydrocarbon was converted into liquids of a polymeric nature. These were separated as efficiently as possible into fractions each containing one polymer. The lowest fraction boiled at 110° to 115° C. and was apparently a dimer although attempts to prove its structure by oxidation methods were fruitless.

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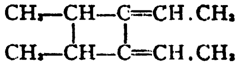
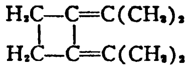
[205] I. G. Farbenindustrie A.-G., French Patent 681,677, 1929; *Chem. Abs.*, 1930, 24, 4343.
[205a] U. S. Patent 1,891,079, Dec. 13, 1932; assigned to Pure Oil Co.; *Brit. Chem. Abs.* **B**, 1933, 755.
[205b] U. S. Patent 1,545,927, July 14, 1925; assigned to Standard Development Co.; *J.S.C.I.*, 1925, 44, 778B.
[206] The polymerization of acetylene, as well as vinyl compounds, is discussed in Chapter 28.
[207] Lebedev and Mereshkowski, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1249; *Chem. Abs.*, 1914, 8, 320.
[208] Lebedev and Mereshkovski, *loc. cit.*

Polymerization of the two dimethylallenes and also of trimethylallene and tetramethylallene has been carefully investigated by Lebedev and Mereshkovski,[210] who have shown that dimerization results in the production of cyclobutane derivatives. Polymerization of symmetrical dimethylallene by heating at 150° C. in the absence of catalysts, was complete in 4 to 5 days and the products consisted of 90 per cent of a dimer (boiling point 163° C.) and 5 per cent of an odorless liquid trimer (boiling point 108° to 110° C. at 17 mm. pressure). The dimer was proved to be 1,2-dimethyl-3,4-diethylidene-cyclobutane, of which the graphic formula is:



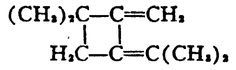
Three isomeric dimers were obtained by Lebedev[211] by heating unsymmetrical dimethylallene in sealed tubes at 100° to 225° C. for 2 to 20 days. The suggested structures of the polymers so produced are shown by the following formulas:

I



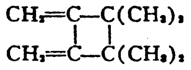
colorless liquid of aromatic odor; b.p. 179°-181° C. at 753 mm.

II



colorless liquid with a kerosene-like odor; b.p. 149°-150° C. at 753 mm.

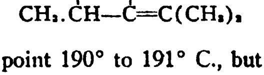
III



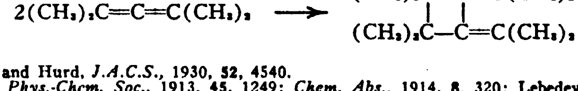
colorless liquid of terpene-like odor; b.p. 140°-141° C. at 753 mm.; very readily polymerized.

At 130° C. the relative amounts of the polymers produced from dimethylallene were: 40 per cent of dimer I, 18 per cent of II, 3 per cent of III, 33 per cent of a trimer boiling at 100° C. at 8 mm. and 6 per cent of a petrolatum-like residue.

When trimethylallene was heated in a sealed tube at 150° C. both polymerization and isomerization reactions occurred. The mixture of dimers formed consisted mainly of the hydrocarbon:



a colorless liquid of boiling point 190° to 191° C., but about 10 per cent of higher polymers were also produced.[212] Similarly, tetramethylallene, on heating, condensed to the dimeric form:



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[209] Meinert and Hurd, *J.A.C.S.*, 1930, 52, 4540.

[210] *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1249; *Chem. Abs.*, 1914, 8, 320; Lebedev, *ibid.*, 1913, 45, 1357; *Chem. Abs.*, 1915, 9, 799. For the rate of polymerization of allene hydrocarbons see Gapon, *ibid.*, 1930, 62, 1385; *J. Gen. Chem. Russia*, 1931, 1, 770, 779; *Brit. Chem. Abs.* A, 1932, 232; *Chem. Abs.*, 1931, 25, 2968; *ibid.*, 1932, 26, 3229, 4580.

[211] *J. Russ. Phys.-Chem. Soc.*, 1911, 43, 820, 1735; *Chem. Abs.*, 1912, 6, 478, 1373; Lebedev and Mereshkovski, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1249.

[212] Lebedev and Mereshkovski, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1249.

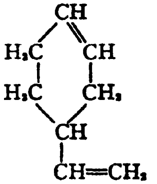
The stability of the methylallenes diminishes with increasing number of methyl groups[213] and the substituted allenes show great tendency to isomerize to the corresponding isomeric acetylene hydrocarbons under the influence of catalysts, such as sodium.

CONJUGATED DIENES

A vast amount of work has been carried out on the conversion of the diolefins into synthetic rubber-like substances. The large number of proposed processes testifies to the great commercial interest in the production of synthetic rubber from these sources. Before presenting a brief summary of this aspect of the polymerization of conjugated dienes, it is well to consider the formation of the simpler liquid polymers of these hydrocarbons. Liquid polymers are frequently formed during the polymerization of 1,3-dienes by heat and other agents, and a study of their properties suggests that many of them are not intermediate products of rubber formation but are formed by polymerization reactions unlike those which result in the formation of rubber-like materials.

It appears that the maximum production of high molecular weight and rubber-like polymers is obtained by carrying out the polymerization at the lowest possible temperatures. Thus, it has been shown that in the case of isoprene and 2,3-dimethylbutadiene, with increasing temperature the proportion of dimers increases and that of the higher polymers diminishes.

The diolefin, 1,3-butadiene, undergoes polymerization to high molecular weight substances when heated to above 90° to 100° C. in an autoclave with or without a catalyst. When heated in a sealed tube at 150° C. for 10 days, butadiene yielded a dimer as well as resinous materials. This dimer, which is a liquid of sharp mustard-like odor and boiling point 129.5° to 130.5° C. at 760 mm., probably has the constitution



since it is hydrogenated to ethylcyclohexane and with bromine forms a tetrabromide.[214] Harries[215] studied the dimer produced from butadiene by heating under pressure and concluded from ozonization experiments that it was identical with 1,5-cyclooctadiene.[216] Vinylcyclohexenes or other oily polymerization products are said to be produced by heating butadiene or its homologues to 400° C. or higher, with or without catalysts.[217]

A kinetic study of the thermal polymerization of butadiene in the vapor phase in pyrex tubes in the temperature range 326° to 436° C. and at pressures of 720 to 1.5 mm. has been made by Vaughan.[218] The reaction was found to be homogeneous and strictly bimolecular over the greater part of its duration. The presence of oxygen in the reacting gas did not accelerate the polymerization rate. The second order velocity constants, k, were related to the temperature, T, by the expression

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[213] Mereshkovski, *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1940; *Chem. Abs.*, 1914, **8**, 1420.

[214] Lebedev, *J. Russ. Phys.-Chem. Soc.*, 1911, **43**, 820, 1735; *Chem. Abs.*, 1912, **6**, 478, 1373; Lebedev and Skavronskaya, *J. Russ. Phys.-Chem. Soc.*, 1911, **43**, 1124; *Chem. Abs.*, 1912, **6**, 855; *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1296; *Chem. Abs.*, 1915, **9**, 798.

[215] *Z. angew. Chem.*, 1912, **25**, 1457; *Chem. Soc. Abs.*, 1912, **102** (1), 706; *Chem. Ztg.*, 1912, **36**, 654; *Chem. Abs.*, 1912, **6**, 2331; Hofmann, *Z. angew. Chem.*, 1912, **25**, 1462; *Chem.-Ztg.*, 1912, **36**, 655; *Chem. Abs.*, 1912, **6**, 2331.

[216] Constitution of this compound was proved by Harries, *Ber.*, 1908, 41, 671.

[217] I. G. Farbenindustrie A.-G., British Patent 343,116, 1929; *Brit. Chem. Abs.*, **B**, 1931, 579.

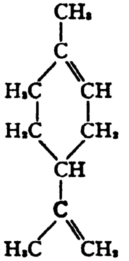
[218] *J.A.C.S.*, 1932, **54**, 3863.

$$\log_{10} k = -5680\left(\frac{1}{T}\right) + 7.673$$

k being expressed in liters per mole per second. The energy of activation is calculated as about 25,000 calories.

Liquid polymerization products are said to be obtained as sole products by heating butadiene above 40° C. under a pressure of 200 atmospheres[219] with aliphatic or aromatic amines or finely divided metals and in the presence of a diluent. A colorless oil may be obtained from butadiene at 150° to 220° C. and a more viscous oil at temperatures above 220° C. The oil may be employed to improve the adhesion of lacquers and binding agents such as glue.

In the polymerization of *isoprene* (2-methyl-1,3-butadiene) at least two dimers appear to be formed, one of which is the well-known hydrocarbon dipentene, having the constitution:



Various divergent opinions concerning the identity of the second dimer have been advanced. By the carefully controlled thermal polymerization of isoprene, Harries[220] obtained a rubber-like substance together with dipentene and a dimer which he regarded as 2,6-dimethyl-1,5,7-octatriene. Similarly, Ostromislensky and Koshelev[221] obtained a hydrocarbon which they called β-myrcene and regarded as an open-chain triene, by heating isoprene at 80° to 90° C. for 3 days. Another dimer, prepared by Aschan,[222] by the autopolymerization of isoprene and called "diprene," corresponded to a m-menthadiene. Wagner-Jauregg[223] indicated that the so-called octatriene of Harries contains only two double bonds and can be catalytically reduced to m-menthane; and also that Ostromislensky's β-myrcene is identical with the m-menthadiene (diprene) of Aschan. The identity of these hydrocarbons with the octatriene of Harries is regarded as established since, like them, it affords carvestrene dihydrochloride on treatment with hydrogen chloride in acetic acid. It appears, therefore, that at least two dimers are formed from isoprene, namely, dipentene and a m-menthadiene of the following constitution (proposed by Lebedev and Mereshkovski[224]):

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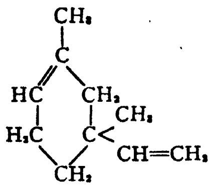
[219] I. G. Farbenindustrie A.-G., British Patent 328,908, 1929; *Brit. Chem. Abs.* B, 1930, 754.
[220] *Ann.*, 1911, 383, 157; *Chem. Abs.*, 1911, 5, 3519.
[221] *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 1928; *Chem. Abs.*, 1916, 10, 1947.
[222] *Ann.*, 1924, 439, 221; *Chem. Abs.*, 1925, 19, 52; *Ber.*, 1924, 57, 1959.
[223] *Ann.*, 1931, 488, 176; *Brit. Chem. Abs.* A, 1931, 1031.
[224] *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1249.



According to Wagner-Jauregg, this m-menthadiene or β-myrcene is the sole dimer formed by heating isoprene at 80° to 90° C. for several days. Lebedev observed that when isoprene was heated in sealed tubes at 150° C. for 6 to 7 days, both dipentene and the isomeric dimer, which boiled at 160° to 161° C., are formed, together with resinous substances.

Whitby and Crozier[225] found that the polymerization of pure isoprene at temperatures of 10° to 145° C. does not afford a polymerizable dimer such as the β-myrcene of Ostromislensky. The products isolated by these investigators were oily cyclic dimers, which are not intermediate steps in the conversion of isoprene into rubber-like polymers. Dipentene was shown to be present in considerable proportion in these oils, together with one or more oily cyclic dimers. Certain inorganic salts, such as antimony pentachloride or tin tetrachloride polymerize these dimers rapidly in the cold, with the production of polymers which may be isomers of the ordinary synthetic caoutchouc.

Gapon[226] stated his belief that the primary polymerization reactions of diolefins occur by the production of activated molecules which can then react with unactivated molecules but not with other activated molecules. The possible number of dimers produced is therefore a function of the number of activated types capable of being formed. The initial activation step is believed to consist in the breaking of one double bond with the momentary production of tervalent carbon atoms. The rate of polymerization of isoprene in sealed tubes at temperatures of 100°, 110°, 130° and 150° C. in the dark was also studied by Gapon.[227] It was concluded that, in the activation of isoprene, three active forms are produced which, by addition to inactivated isoprene molecules, lead to the formation of dipentene, 1,3-dimethyl-3-vinyl-6-cyclohexene, and two polymers.

The polymerization of isoprene and similar conjugated diolefins under the influence of catalysts takes place very readily at low temperatures and usually results in the production of rubber-like polymers of high molecular weight. A full discussion of the specific action of various polymerizing catalysts is beyond the scope of this work but mention may be made of the following materials which are active in promoting low-temperature polymerization of these hydrocarbons: anhydrous inorganic halides such as aluminum chloride[228]; tin tetrachloride, antimony pentachloride, boron trifluoride[229]; strong acids, metals or oxides,[230] ozonides and peroxides[231] of the alkalies or alkaline earths. In addition to these well-known polymerizing agents, many apparently unrelated materials have been stated to catalyze the polymerization of dienes, for example, alkaline earth alkyls,[232] glycerol, starch, urea, and caoutchouc-like substances.[233]

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[225] *Canad. J. Research*, 1932, **6**, 203; *Brit. Chem. Abs.* **A**, 1932, 361.

[226] *J. Russ. Phys.-Chem. Soc.*, 1930, **62**, 1385; *Chem. Abs.*, 1931, **25**, 2968.

[227] *J. Russ. Phys.-Chem. Soc.*, 1930, **62**, 1395; *Chem. Abs.*, 1931, **25**, 2968.

[228] E.g., Bataafsche Petroleum Maatschappij, British Patent 358,068, 1931; *Brit. Chem. Abs.* **B**, 1932, 172; see Chapter 5 for examples of other catalytic materials.

[229] Farbenfabrik vorm. F. Bayer und Co., German Patent 264,925, 1912; *Chem. Abs.*, 1914, **8**, 267.

[230] For example, butadiene is polymerized in the presence of sodium balls of 1.1 mm. diameter by Ebert, Fries and Garbsch (U. S. Patent 1,880,918, Oct. 4, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 514). In the polymerization of diolefins by alkali or alkaline earth metals, alkali metal hydrides, or organometallic compounds, additions of dioxan or substances capable of substituting the metallic atoms of organometallic compounds, such as thiophene, hydrocyanic acid, benzyl cyanide and methylacetylene are of advantage, according to Ebert and Fries (U. S. Patent 1,832,450, Nov. 17, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 1157; I. G. Farbenindustrie A.-G., French Patent 710,791, 1931; *Chem. Abs.*, 1932, **26**, 1615). See also Ebert, Fries and Reppe, U. S. Patent 1,827,285, Oct. 13, 1931; *Chem. Abs.*, 1932, **26**, 479; French Patents 688,592 and 688,593, 1930; *Chem. Abs.*, 1931, **25**, 710; all patents assigned to I. G. Farbenindustrie A.-G.

The catalytic influences of peroxides, per-acids, and oxidized substances formed during autoxidation of diolefins, on the polymerization of isoprene and its congeners has been known for many years.[234] Conant and Tongberg[235] showed that the rate of polymerization of isoprene under high pressure is greatly increased by the presence of ozonized isoprene. The rate is approximately in accord with a first order reaction probably because of an autocatalytic effect. From experiments on the polymerization of isoprene, dimethylbutadiene, cyclopentadiene, myrcene, and other hydrocarbons in the presence of oxygen at 80° C., Staudinger and Lautenschläger[236] concluded that in all cases autoxidation accelerates polymerization. Though addition of peroxides catalyzes polymerization, the result is not as great as with oxygen, hence the active agent is probably a compound resulting from the autoxidation.

Increase of pressure increases the velocity of the (uncatalyzed) polymerization of isoprene, dimethylbutadiene, and other diolefins, and also reduces the temperature of initial polymerization. The reaction was found by Tammann and Pape[237] to follow the unimolecular law. This suggested that before union the molecules undergo some change and that the speed of the complete process is determined by the rate of this initial reaction.[238]

The other methylated derivatives of butadiene, most important of which are piperylene (1-methylbutadiene) and 2,3-dimethylbutadiene can be polymerized more or less readily to rubber-like polymers. Certain other dienes, such as 1,1-dimethylbutadiene, 1-phenylbutadiene, 1,2,3,4-tetramethylbutadiene, and 1,2-dimethylbutadiene, also possess a great tendency to polymerize but the products are not rubber-like. An increase in the number of methyl substituents in butadiene diminishes the ease of polymerization. Methyl substitution in the terminal carbon atoms, compared with substitution in the middle positions, also exerts an unfavorable influence on the polymerization to high molecular weight products.[239] The introduction of phenyl groups into the butadiene chain favors polymerization to dimers but inhibits further polymerization to rubber-like or resinous polymers.[240]

Very few of the simple polymers of these higher conjugated dienes have been definitely identified. A dimer of 2,3-dimethyl-1,3-butadiene closely resembling dipentene, can be produced by careful polymerization of that diene or by thermal depolymerization of 2,3-dimethylbutadiene rubber.[241] According to Lebedev and Mereshkovski,[242] this dimer, boiling at 85° C. at 13 mm. and at 205° C. at 750 mm., with a density 0.8741, probably possesses the structure:

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[231] Holt, *Z. angew. Chem.*, 1914, **27**, 153; Holt and Steimmig, U. S. Patent 1,189,110, June 27, 1916; *Chem. Abs.*, 1916, **10**, 2162. The polymerization of vinyl esters with these catalysts is described, for example, by Klatte and Rollett, U. S. Patent 1,241,738, Oct. 2, 1917; *Chem. Abs.*, 1918, **12**, 231; Chemische Fabrik Griesheim-Elektron, German Patent 281,688, 1914; *J.S.C.I.*, 1915, **34**, 623.

[232] Badische Anilin- und Soda-Fabrik, German Patent 255,786, 1912; *Chem. Abs.*, 1913, **7**, 1815.

[233] Farbenfabrik vorm. F. Bayer und Co., German Patent 248,399, 1911; *Chem. Abs.*, 1912, **6**, 2856.

[234] *Cf.* Engler. *Repts. 8th Int. Congr. Appl. Chem.*, 1912, **25**, 661.

[235] *J.A.C.S.*, 1930, **52**, 1659.

[236] *Ann.*, 1931, **488**, 1; *Chem. Abs.*, 1931, **25**, 5138.

[237] *Z. anorg. Chem.*, 1931, **200**, 113; *Brit. Chem. Abs.* **A**, 1931, 1239.

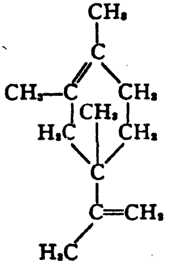
[238] *Cf.* Gapon, *J. Russ. Phys.-Chem. Soc.*, 1930, **62**, 1395; *Chem. Abs.*, 1931, **25**, 2968; *J. Gen. Chem. Russia*, 1931, 1. 496; *Chem. Abs.*, 1932, **26**, 4580.

[239] Macallum and Whitby, *Trans. Roy. Soc. Canada*, 1928, **22**, 39; *Chem. Abs.*, 1928, **22**, 2080.

[240] Whitby and Gallay, *Canad. J. Research*, 1932, **6**, 280; *Chem. Abs.*, 1932, **26**, 3479.

[241] Kondakov, *J. prakt. Chem.*, 1901, **2** (64), 109; *Chem. Soc. Abs.*, 1901, **80** (1), 625; Richard, *Compt. rend.*, 1911, **153**, 116; *Chem. Abs.*, 1911, **5**, 3227.

[242] *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1249; *Chem. Abs.*, 1914, **8**, 320.



The diolefins which do not possess a conjugated system of double bonds are much more resistant to polymerization than those of the butadiene type. Thus, diallyl (1,5-hexadiene),

$$CH_2{=}CH.CH_2.CH_2.CH{=}CH_2$$

was completely unchanged by heating for 8 days at 140° to 200° C., but heating for 10 days at 250° C., 40 per cent of the hydrocarbon became converted into polymers and isomerization also occurred. The crude product of the reaction contained about 15 per cent of a liquid dimer (boiling point 97°-98° C. at 20 mm.) and 85 per cent of a colorless insoluble resinous polymer.[243]

Whitby and Gallay[244] prepared a number of dimers of various substituted butadienes by the action of heat on these hydrocarbons. Besides higher polymers the dimers given in Table 113 were obtained:

TABLE 113.—*Dimers of Substituted Butadienes.*

Parent Diolefin	Boiling Point ° C.	Boiling Point of Dimers ° C.
2,3-Dimethylbutadiene	69–70	95 at 17 mm.
1,2-Dimethylbutadiene	80–82	(1) 97–100 at 16 mm.
		(2) 108–110 at 16 mm.
1,1-Dimethylbutadiene	76–77	(1) 94–97 at 16 mm.
		(2) 105–108 at 16 mm.
1,3-Dimethylbutadiene	76–77	90–92 at 16 mm.
1,4-Dimethylbutadiene	—	(1) 90 at 20 mm.
		(2) 96–98 at 20 mm.

Tetramethylbutadiene shows no tendency to polymerize on heating under conditions which readily convert isoprene to rubber-like material, but a dimer may be produced by the action of sulphuric acid.[245] The cyclic conjugated diolefins as a class are very readily polymerized, the usual products being high molecular weight resinous polymers, though the lower polymers are also formed under favorable conditions.

Cyclopentadiene is remarkable for its ease of polymerization and for the large number of polymers which have been prepared, though the question of the constitution of these compounds has aroused considerable controversy. The polymerization of cyclopentadiene to solid polymers proceeds spontaneously on standing at ordinary temperature, particularly in the presence of air or oxygen, but is much more rapid at higher temperatures.[246] Exposure to light has little influence on the reaction.[247] When cyclopentadiene is heated to 135° C., dicyclopentadiene is formed mainly, but by prolonging the heat treatment and by using somewhat higher temperatures, Staudinger and his collaborators[248] have been able to prepare a whole series of polymers which include the dimer, trimer, tetramer, pentamer and also possibly a hexamer.

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[243] Lebedev and Mereshkovski, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1249; *Chem. Abs.*, 1914, 8, 320.

[244] *Canad. J. Research*, 1932, 6, 280; *Chem. Abs.*, 1932, 26, 3479.

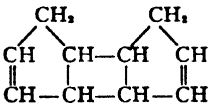
[245] Macallum and Whitby, *Trans. Roy. Soc. Canada*, 1928, 22, 39; *Chem. Abs.*, 1928, 22, 2080; *cf.* Whitby and Gallay, *loc. cit.*

These polymers, the first four of which are crystalline solids, may be separated from one another by fractional distillation *in vacuo*. Each compound possesses two double bonds and the corresponding dihydro- and tetrahydro-derivatives are readily obtained by catalytic hydrogenation. Perhaps the most remarkable feature of this series of polymers is the reversible character of the polymerization process. When heated at atmospheric pressure the polymers are partly dissociated to yield cyclopentadiene and the other (lower) polymers. Dicyclopentadiene yields mainly cyclopentadiene by distilling at atmospheric pressure, but tricyclopentadiene is more stable to heat than either dicyclopentadiene or tetracyclopentadiene. The melting points of these polymers are given in Table 114:

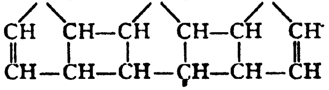
TABLE 114.—*Polymers of Pentadiene.*

Compound	Melting Point ° C.
Dicyclopentadiene	32.5 α-form 19.5 β-form
Tricyclopentadiene	60
Tetracyclopentadiene	188–190
Pentacyclopentadiene	270
Polycyclopentadiene	decomposes above 300

The question of the chemical constitution of these crystalline lower polymers of cyclopentadiene appears to be undecided. If 1,2 addition takes place, the constitution of dicyclopentadiene can be represented by the graphic formula



This formula, first proposed by Kraemer and Spilker,[249] is also supported by Staudinger and Rheiner,[250] who assign to tricyclopentadiene the constitution



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[246] Roscoe, *J.C.S.*, 1885, **47**, 669; *Ann.*, 1886, **232**, 348; *Chem. Zentr.*, 1886, 449; Etard and Lambert, *Compt. rend.*, 1891, **112**, 945; *Chem. Soc. Abs.*, 1891, **60**, 1085; Kronstein, *Ber.*, 1902, **35**, 4150; Stobbe and Reuss, *Ann.*, 1912, **391**, 151; *Chem. Abs.*, 1912, **6**, 3275; Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436.

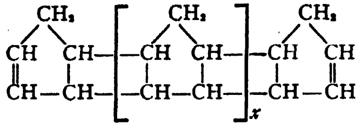
[247] Stobbe and Reuss, *Ann.*, 1912, **391**, 151.

[248] Staudinger and Rheiner, *Helv. Chim. Acta*, 1924, **7**, 23; *Chem. Abs.*, 1924, **18**, 1275; Staudinger and Bruson, *Ann.*, 1926, **447**, 97; *Chem. Abs.*, 1926, **20**, 2148; *Ind. Eng. Chem.*, 1926, **18**, 381; Bruson, Dissertation, Zürich, 1925.

[249] *Ber.*, 1896, **29**, 552; see also *Ber.*, 1890, **23**, 3283.

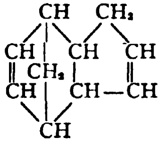
[250] *Loc. cit.*

On this basis the general formula for the non-resinous polymers of cyclopentadiene becomes

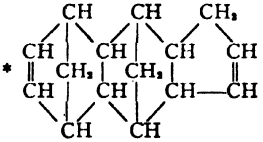


where *x* is a relatively small integer. The depolymerization of these cyclopentadiene polymers is considered to take place by rupture of the cyclobutane ring systems under the influence of heat.

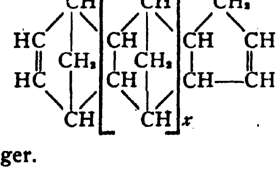
An alternative formula for dicyclopentadiene is that originally proposed by Wieland,[251] namely,



which may be regarded as the result of the addition of a cyclopentadiene molecule activated in the 1,4 position to a second molecule at the 1,2 position. A good deal of evidence in support of this configuration for dicyclopentadiene, and of similar structures for the other polymers, has been put forward by Alder, Stein and Finzenhagen,[252] who found that dicyclopentadiene readily yields an addition compound with phenyl azide and oxidation of its dihydro-derivative affords cyclopentane-1,3-dicarboxylic acid. Later, Alder and Stein [253] showed that tricyclopentadiene and tetracyclopentadiene also form addition compounds with phenyl azide and adduced evidence in support of the contention that tricyclopentadiene is also formed by 1,4- addition of cyclopentadiene to dicyclopentadiene and thus possesses the configuration



Polymerization can continue indefinitely on account of the highly reactive ethylene linkage (marked *) and the general formula of the higher polymers, on the basis of this mode of coupling, can be written as



where *x* is a small integer.

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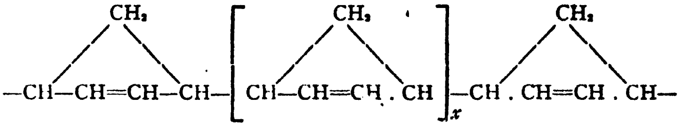
[251] *Ber.*, 1906, **39**, 1492.

[252] *Ann.*, 1931, **485**, 223; *Brit. Chem. Abs.* **A**, 1931, 473. The stereochemistry of cyclopentadiene polymerization is discussed by Alder, Stein, Eckhardt, von Buddenbrock and Schneider, *Ann.*, 1933, **504**, 216; *Brit. Chem. Abs.* **A**, 1933, 941.

[253] (With Reese and Grassmann), *Ann.*, 1932, **496**, 204; *Brit. Chem. Abs.* **A**, 1932, 938.

HIGHER POLYMERS OF CYCLOPENTADIENE

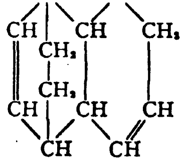
Another and different type of condensation occurs when cyclopentadiene is polymerized in the presence of catalysts such as anhydrous metallic halides. There is produced a white amorphous powder of the formula $(C_5H_6)_x$, in which x may vary from 20 to 100. When dried at 50° C. in a high vacuum it swells to a spongy brittle mass which can be powdered. This so-called "cyclopentadiene rubber" takes up oxygen on exposure to air and shows other evidences of being unsaturated. The probable structure of this material is:[254]



The polymerization of cyclopentadiene to this resinous material has been investigated by Staudinger and Bruson.[255] The following substances were found effective as catalysts: the halides of the amphoteric elements such as the tetrahalides of tin and titanium, the tri- and pentahalides of antimony, boron trichloride, arsenic halides, ferric and bismuth halides and also certain strongly negative substances such as sulphuryl chloride, phosphorus pentoxide and phosphorus pentachloride. The reaction is so rapid in the case of tin tetrachloride[256] (the best catalyst found) and of antimony pentachloride and boron trichloride, that it was necessary to use a liquid diluent, such as benzene, chloroform and carbon tetrachloride, and to cool vigorously.

CYCLOHEXADIENE

The work of Hofmann and Damm[257] on *1,3-cyclohexadiene* indicates that this hydrocarbon exhibits considerably less tendency to polymerize than butadiene or its 2- or 3-substituted homologues, thus it is more closely related to 1- and 4-substituted butadienes. Sodium is without influence on this compound, though ferric chloride exerts a pronounced accelerating action on its polymerization. On heating at 200° to 220° C. for several hours the hydrocarbon is largely polymerized with the production of a solid rubber-like polymer ("dihydrobenzene rubber") and a terpenic dimer. Practically no polymerization occurs at temperatures below about 120° C. The dimeric cyclohexadiene differs from the corresponding dimer of cyclopentadiene in that the former cannot be solidified in a freezing mixture and is not decomposed when boiled at atmospheric pressure. To this dimer, which contains two ethylenic linkages and is resinified by concentrated sulphuric and nitric acids, Hofmann and Damm assigned the constitution,



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[254] Bruson and Staudinger, *Ind. Eng. Chem.*, 1926, **18**, 381.
[255] *Ind. Eng. Chem.*, 1926, **18**, 381; *Ann.*, 1926, **447**, 110; *Chem. Abs.*, 1926, **20**, 2148.
[256] U. S. Patent 1,720,929, July 16, 1929; *Brit. Chem. Abs.* **B**, 1929, 972.
[257] *Mitt. schlesischen Kohlenforsch. Kaiser-Wilhelm Ges.*, 1925, **2**, 97; *Chem. Zentr.*, 1926, **1**, 2342; *Chem. Abs.*, 1928, **22**, 1249.

This structure has been confirmed by Alder and Stein[258] by oxidation of the corresponding dihydro-derivatives to cis-hexahydroterephthalic acid.

Cyclohexadiene gives tars immediately when treated with sulphuric acid.[259]

Cyclohexene, when treated with 96 per cent sulphuric acid at 2° to 5° C., yielded 37 per cent of an oil. From this oil Nametkin and Abakumovskaja[260] obtained three fractions, which consisted of (1) a hydrocarbon, $C_{12}H_{22}$, boiling at 216°-219° C. at 739 mm., which gave a small amount of naphthalene on dehydrogenation; (2) a hydrocarbon, $C_{18}H_{32}$, which boiled at 145°-147° C. at 1.5-2 mm.; and (3) a hydrocarbon, $C_{24}H_{20}$, with one unsaturated linkage which was a very viscous liquid and boiled at 200°-203° C. at 1.5-2 mm.

MUTUAL CONDENSATION OF OLEFINS AND DIOLEFINS

Closely allied with the polymerization process proper is the condensation of two different unsaturated hydrocarbons with the production of a more complex molecule. Both types of reaction are essentially the same, and both owe their occurrence to the unsaturated linkages present in the hydrocarbons reacting. The condensation of a conjugated diolefin hydrocarbon with various monolefin hydrocarbons, a reaction which was also noted by Aschan,[261] has been utilized as a source of new synthetic resinous materials. Thomas and Carmody[262] observed that, though the polymerization of pure isoprene in the presence of anhydrous aluminum chloride was slow at ordinary temperature, the addition of an olefin, such as 2-pentene or trimethylethylene, caused a reaction to commence immediately. Two types of polymers were obtained by decomposing the aluminum chloride complex with water: namely, a white granular resin of the formula $(C_5H_8)_x$, insoluble in most organic solvents, together with a light straw-colored resin soluble in many organic solvents and with a carbon-hydrogen ratio which varied with the relative proportions of diolefin and monolefin employed. The insoluble resin is evidently a polymer derived mainly, if not entirely, from the polymerization of the isoprene, whereas the soluble product is probably the result of mutual condensation of diolefin and monolefin. The yield of the soluble polymer is a function of the proportion of monolefin present though its hardness is inversely proportional to that amount. On the other hand, the amount of insoluble polymer is an inverse function of the monolefin present in the diolefin-monolefin mixture. The production of resins for use, for example, in varnish formulation, by the action of aluminum chloride on cooled highly unsaturated cracked distillates containing both diolefin and monolefin constituents, has been carried out by Thomas and Carmody.[263] Thomas and Hochwalt[264] described a process for the production of a non-acid, unsaponifiable resin by subjecting a cracked distillate, which boils below 180° C. and contains 25 to 50 per cent of olefins and diolefins, to the action of aluminum chloride. The product is treated with water and distilled to remove volatile constituents. The residue is dissolved in a hydrocarbon and the resin is then precipitated from the solution by the addition of alcohol and acetone.

Hugh[265] obtained a material resembling rubber or deresinated gutta percha, by polymerizing at 20° to 201° C. a mixture of a diolefin (butadiene, isoprene, or dimethylbutadiene) and an aromatic olefin (styrene, naphthylethylene, divinylbenzene, or their homologues) in the presence of sodium, sodium-amalgam, or other catalyst, and also, if necessary, of an antioxidant such as phenyl-α- or β-naphthylamine. A non-volatile hydrocarbon swelling agent may be added to render the product thermoplastic. These materials are intended for use in the insulation of submarine cables.[266]

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[258] *Ann.*, 1932, **496**, 197; *Chem. Abs.*, 1932, **26**, 5093.

[259] Baeyer, *Ann.*, 1894, **278**, 88.

[260] *J. Gen. Chem. Russ.*, 1932, **2**, 608; *Chem. Abs.*, 1933, **27**, 1620; *Ber.*, 1933, **66**, 358.

[261] *Öfversigi Finska Vetenskaps Soc.*, 1916, **58**, 42; *Chem. Abs.*, 1920, **14**, 3823.

[262] *J.A.C.S.*, 1932, **54**, 2480; see also Chapter 6.

[263] *Ind. Eng. Chem.*, 1932, **24**, 1125.

[264] U. S. Patent 1,836.629, Dec. 15, 1931; assigned to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1932, **26**, 1144; Thomas and Hochwalt Laboratories, Inc., French Patent 679,402, 1929; *Chem. Abs.*, 1930, **24**, 3915; British Patent 340,001, 1929; *Chem. Abs.*, 1931, **25**, 2867.

[265] British Patent 345,939, 1929; assigned to Standard Telephones and Cables, Ltd.; *Brit. Chem. Abs.* **B**, 1931, 710.

THE PRODUCTION OF SYNTHETIC RUBBER

The fact that isoprene, prepared by the destructive distillation of rubber, could be converted to spongy elastic material closely resembling natural rubber was observed by Williams [267] and, 19 years later, by Bouchardat.[268] The latter investigator employed hydrochloric acid as the condensing material. The credit of first actually synthesizing an artificial rubber-like material belongs, however, to Tilden.[269] Tilden found that hydrochloric acid and also nitrosyl chloride were effective in promoting polymerization of synthetic isoprene to rubber-like materials. He noted later that, under the influence of light, polymerization also resulted. Tilden stated that the action of hydrochloric acid on isoprene converts it partially into caoutchouc. The latter seems to be produced most readily from the oily polymer, resulting from the action of heat. This important fact was completely substantiated later by Ostromislensky and Koschelev,[270] who found that the character of the synthetic isoprene rubber was markedly influenced by its mode of polymerization, for, on heating isoprene to 80° to 90° C., it was found to polymerize spontaneously to a dimer called β-myrcene, which then yielded a normal isoprene caoutchouc when polymerized with sodium and barium peroxides at 60° to 70° C., whereas isoprene itself, when treated with these reagents, gave an abnormal caoutchouc product.

The polymerization of 2,3-dimethyl-1,3-butadiene (diisopropenyl), a homologue of isoprene, to a rubber-like product was effected by Kondakov [271] by subjecting this hydrocarbon to the action of alcoholic potash for three days. Kondakov also observed that the polymerization of this unsaturated hydrocarbon occurred spontaneously and was much more rapid than the polymerization of isoprene or butadiene. During the polymerization of this hydrocarbon, either spontaneously or under the influence of alcoholic potash, dimers and trimers were formed also. Like natural Para rubber, Kondakov's rubber can be depolymerized by heat to yield a dimer of 2,3-dimethyl-1,3-butadiene, identical with the product obtained by the careful polymerization of 2,3-dimethyl-1,3-butadiene.

The rapid conversion of unsaturated hydrocarbons to rubber-like substances was also reported by Wallach [272] and Lebedev,[273] with daylight; by Ostromislensky,[274] with ultraviolet radiation; and by Collie,[275] who employed the silent electric discharge.

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[266] See also Le Matériel Téléphonique Soc. anon.; French Patent 707,692, 1930; *Chem. Abs.*, 1932, **26**, 734.

[267] *Proc. Royal Soc.*, 1860, 10. 516; *Phil. Trans.*, 1860, 245; *Jahresber.*, 1860, 495.

[268] *Compt. rend.*, 1879, **89**, 1117; *Chem. Soc. Abs.*, 1880, **38**, 323.

[269] *Chem. News*, 1882, **46**, 120; *Chem. Soc. Abs.*, 1883, **44**, 75. *Jahresber.*, 1882, 406. *J.C.S.*, 1884, **45**, 410; *Chem. News*, 1892, **65**, 265; *Chem. Soc. Abs.*, 1892. **62**, 1482; *Ber.*, 1892, **25**, Ref. 644.

[270] *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1928; *Chem. Soc. Abs.*, 1916, **110** (1), 274; *cf.* Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, 1916, **48**, 1071; *Chem. Soc. Abs.*, 1917, **112** (1), 399.

[271] *J. prakt. Chem.*, 1901, (2) **64**, 109; *Chem. Soc. Abs.*, 1901, **80** (1), 625; *cf.* Hofmann, Delbrück and Meisenburg, U. S. Patent 1,178,721, April 11, 1916; *Chem. Abs.*, 1916, **10**, 1718; Hofmann and Delbrück, U. S. Patents 1,081,613 and 1,081,614, Dec. 16, 1913; *Chem. Abs.*, 1914, **8**, 585.

[272] *Ann.*, 1887, **238**, 78; *Chem. Soc. Abs.*, 1887, **52**, 595.

[273] *J. Russ. Phys.-Chem. Soc.*, 1909, 41, 1868; *cf. ibid.*, 1910, **42**, 949; *Chem. Soc. Abs.*, 1911, **100** (1), 26.

[274] *J. Russ. Phys.-Chem. Soc.*, 1912, **44**, 204; *Chem. Soc. Abs.*, 1912, **102** (1), 280; *Chem.-Ztg.*, 1912, **36**, 199; *Chem. Abs.*, 1912, **6**, 2184. Danish Patent 16,533, 1912; *Chem. Abs.*, 1913, **7**, 1299. German Patent 264,123, 1912; *Chem. Abs.*, 1914, **8**, 267. British Patent 6,300, 1912; *Chem. Abs.*, 1913, **7**, 3038.

The rise in the price of natural rubber after 1905, which resulted from the greatly increased demand for this material, stimulated research on the polymerization of dienes to rubber-like materials. In 1911, Harries [276] reported that the polymerization of isoprene to rubber-like substances took place when isoprene was heated in a sealed tube with acetic acid for 8 days at 90° to 100° C., though the yields were variable. Hofmann and Coutelle [277] also observed that pure isoprene or its homologues could be polymerized to caoutchouc in good yield when subjected to heat, with or without catalysts. Perhaps the most important discovery was that of Matthews and Strange [278] (1910), who found that metallic sodium was a very active polymerizing agent. Harries,[276] who appears to have made this same discovery towards the end of 1910, stated that butadiene is converted into synthetic rubber at ordinary temperature in a few hours under the influence of metallic sodium and isoprene is converted at about 60° C. almost quantitatively without the production of dimers or trimers, in from 50 to 100 hours.[279] The sodium is for the greater part quite unchanged. Harries found, however, that the sodium-condensed caoutchouc has a structure differing from that possessed by synthetic rubbers produced by the action of heat or by the aid of acetic acid. Certain other catalytic agents, such as acetic anhydride,[280] perborates, ozonides of isoprene, or other oxygen carriers,[281] sodamide,[282] and sulphur,[283] have also been proposed.

According to Harries,[284] there are three well-known methods of polymerizing butadiene and its simple homologues to rubber-like products, namely, (1) heating alone, or in acetic acid solution, in a sealed tube for a period at 60° to 100° C.; (2) heating, or allowing to stand, in the presence of metallic sodium in an atmosphere of carbon dioxide; and (3) heating in the presence of peroxides, especially benzoyl peroxide.

As regards the quality of the synthetic rubbers produced by the polymerization of the simple butadiene derivatives, it must be clearly borne in mind that though these substances may possess many of the characteristics of natural rubber, they are not identical by any means. Even with the isoprene polymers, the identity with natural rubber is not proved. Harries has attempted to assign structures to natural and synthetic rubbers on the basis of the products obtained by decomposing their ozonides with water.

Briefly, natural rubber or caoutchouc is a transparent tough elastic material, soluble in various organic solvents, and its composition may be expressed by the formula $(C_5H_8)_x$. It is unsaturated in nature and on destructive distillation yields a mixture of hydrocarbons, of which the most important are isoprene and dipentene. When heated with sulphur, or when treated with solutions of sulphur dichloride in carbon disulphide it becomes "vulcanized." This latter important property is also possessed by the synthetic rubbers prepared by the polymerization of diolefins. The synthetic rubbers prepared by the polymerization of dienes under various conditions give rise to ozonides which exhibit different rates of hydrolysis with water and give different decomposition products, According to Harries, 1,3-butadiene, isoprene, and piperylene give rise, on polymerization, to synthetic rubbers which are superior from a practical point of view to those obtained by the polymerization of 2,3-dimethyl-1,3-butadiene, a conclusion also arrived at by Fisher and Chittenden.[285]

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[275] *J.C.S.*, 1905, **87**, 1540.

[276] *Ann.*, 1911, **383**, 157; *Chem. Abs.*, 1911, **5**, 3519.

[277] See, for example, Canadian Patent 143,493, 1912; *Chem. Abs.*, 1913, **7**, 427; *cf.* Canadian Patents 143,489 to 143,492, 1912; *Chem. Abs.*, 1913, **7**, 426. U. S. Patent 1,062,915, May 27, 1913; *Chem. Abs.*, 1913, **7**, 2485; *cf.* U. S. Patents 1,062,828, 1,062,912, 1,062,913, and 1,062,914, May 27, 1913; *Chem. Abs.*, 1913, **7**, 2485. U. S. Patents 1,069,951, 1,070,120 and 1,070,258, Aug. 12, 1913; *Chem. Abs.*, 1913, **7**, 3424. Farbenfabr. vorm. F. Bayer & Co., British Patent 6,540, 1911; *Chem. Abs.*, 1912, **6**, 2548; Addn. 13,931 to French Patent 419,316, 1911; *Chem. Abs.*, 1912, **6**, 2548. German Patent 235,423, 1909; *Chem. Abs.*, 1912, **6**, 2548.

[278] See, for example, British Patent 24,790, 1910; *Chem. Abs.*, 1912, **6**, 1542. German Patent 249,868, 1911; *Chem. Abs.*, 1912, **6**, 3200.

[279] *Cf.* Dubosc, Sealed Note 1012, 1912; *Bull. soc. ind. Rouen*, 1926, **54**, 220; *Chem. Abs.*, 1927, **21**, 673.

[280] See, for example, Chem. Fabrik. auf. Actien vorm. E. Schering, French Patent 433,825, 1911; *Chem. Abs.*, 1912, **6**, 2332.

[281] See, for example, Badische Anilin- und Soda-Fabrik, British Patent 22,454, 1911; *Chem. Abs.*, 1913, **7**, 1109.

[282] See, for example, Hodgkinson, British Patent 9,219, 1910; *J.S.C.I.*, 1911, **30**, 1075.

[283] See, for example, Badische Anilin- und Soda-Fabrik, French Patent 434,587, 1911; *Chem. Abs.*, 1912, **6**, 2332; British Patent 10,914, 1911; *Chem. Abs.*, 1912, **6**, 3026. Holt, U. S. Patent 1,062,973, May 27, 1913; *Chem. Abs.*, 1913, **7**, 2486.

[284] "Untersuchungen über die natürlichen und künstlichen Kautschukarten," Julius Springer, Berlin, 1919, 170.

It appears that, though many diolefins have been stated to polymerize to rubber-like substances, the possibilities are in reality quite limited to simple butadiene derivatives, notably butadiene, isoprene, piperylene (1,3-pentadiene), and 2,3-dimethyl-1,3-butadiene. For example, Harries found that both 1,1-dimethyl-1,3-butadiene and 1-phenyl-1,3-butadiene presented difficulties in polymerization to rubber. Macallum and Whitby[286] concluded that, (1) methyl substitution in the terminal carbon atoms of butadiene, compared with such substitution in the middle positions, exerts an unfavorable effect in the ease of polymerization to rubber-like substances, and (2) an increase in the number of methyl substituents in butadiene diminishes the ease of polymerization. In support of the latter statement it was shown that 1,2,3,4-tetramethyl-1,3-butadiene,

$$H_3CCH{=}C(CH_3){-}C(CH_3){=}CHCH_3$$

had little or no tendency to undergo polymerization to a rubber. Recently Fisher and Chittenden[287] prepared 3-methyl-1,3-pentadiene (1,2-dimethyl-1,3-butadiene),

$$CH_3CH{=}C(CH_3){-}CH{=}CH_2$$

and found that this hydrocarbon did not polymerize to an elastic, resilient, rubber-like product. These workers concluded that the polymerization of dienes to rubber-like products does not depend solely upon the presence of the vinyl group.

It must not be supposed that these and other diolefins cannot be made to polymerize. In actual fact many of these substances polymerize with greater ease than butadiene or its simple homologues, but the products are not rubber-like in nature.

Results of theoretical and practical interest were obtained by Ostromislensky[288] on the polymerization of vinyl bromide, a process which resulted in the production of three polymeric substances which he called *caouprene bromides.* On treatment with zinc dust they yielded a substance apparently identical with the butadiene-rubber of Harries. Similarly the bromide of Harries' butadiene-rubber was found to exist in three modifications, identical or isomeric with the caouprene bromide of Ostromislensky.

Since the World War there has been a renewal of interest in the polymerization of diolefins, produced by the pyrolysis of petroleum hydrocarbons, to rubber-like substances and rubber substitutes. Processes for polymerizing isoprene in which this diolefin is treated, for example, with colloidal suspensions or solu-

[285] *Ind. Eng. Chem.*, 1930, **22**, 869.

[286] *Trans. Roy. Soc. Canada*, 1928, (3) **22**, 39; *Chem. Abs.*, 1928, **22**, 2080. Whitby and Katz (*Ind. Eng. Chem.*, 1933, **25**, 1204, 1338) reviewed the production of synthetic rubber.

[287] *Loc. cit.*

[288] *J. Russ. Phys.-Chem. Soc.*, 1912, **44**, 204; *Chem. Soc. Abs.*, 1912, **102** (1), 280; *Chem. Abs.*, 1912, **6**, 1538.

tions of substances such as egg albumin, sodium oleate, or turkey-red oil, in the presence of electrolytes, together with oxygen or compounds which yield oxygen, such as perborates, have been proposed.[289] The rubber so obtained is rolled into sheets, mixed with sulphur, and vulcanized in the ordinary way, and the products are said to be distinguished by high elasticity and strength.

In another method[290] for the production of rubber-like products, the polymerization of diolefins is effected in the presence of an emulsion which has previously been passed through a homogenizer. Polymerization is thereby facilitated and the yield of rubber-like product is improved. Diolefins in the form of creamy or gelatinous mixtures with aqueous solutions (these mixtures containing at least 75 per cent by volume of the hydrocarbons) also may be polymerized to rubber-like products.[291] Additional substances such as oxidizing agents, buffer mixtures, and materials capable of modifying the surface tension of emulsions may be present also. The polymerization of diolefins likewise can be effected in the presence of latex or similar vegetable saps and of oxidizing or emulsifying agents.[292]

The polymerization of butadiene hydrocarbons with the aid of sodium hydride is slower than with metallic sodium, which sometimes induces polymerization with almost explosive violence.[293] With sodium hydride, it is said that a more homogeneous product is obtained. The process is conveniently conducted in the presence of an indifferent solvent such as benzene, with agitation.

Plastic or elastic products of polymerization with exceptional stability on storage, can be made from diolefins such as isoprene or butadiene, by adding a dissolved or emulsified antioxidant to the latex or latex-like products from which the polymerized material is to be separated.[294] The antioxidant may be introduced before or during coagulation of the latex-like suspension and is used in such proportions that 0.5 to 2 per cent is present in the coagulated product. Prior to coagulation, compounding ingredients also may be introduced.

The polymerization of butadiene or its homologues sometimes leads to rubber-like products which are insoluble in benzene and do not readily become plastic when milled. These undesirable features can be removed by treating with an organic nitro-compound, e.g., mono-, di-, or trinitrobenzene, advantageously in the presence of a solvent such as benzene and at temperatures of about 140° to 150° C.[295]

Since the polymerization of diolefins is sometimes extremely violent, it has been proposed[296] to connect a second chamber, containing no polymerizing catalyst, with the actual reaction vessel. If violent reactions do occur, the starting material distils into the second chamber where it may be returned, e.g., by distillation or by gravity, when convenient, into the reaction vessel.

According to Kleiber and Gilardi[297] an elastic mass, capable of being vulcanized and used as a rubber substitute, is obtained by treating petroleum with an oxidizing agent such as nitric acid or sodium peroxide for several days in the presence of soda-lime or sodium acetate.[298] The liquid is neutralized and repeatedly distilled over colophony. The distillate is treated with dilute alkali and allowed to stand, when three layers are formed. The two upper layers are treated with glacial acetic acid or formaldehyde, together with raw rubber as a catalyst. The mixture is heated to 60° C., and a syrupy substance is obtained from which an elastic substance can be precipitated with acetone or alcohol.

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[289] See, for example, I. G. Farbenindustrie A.-G., British Patents 283,840 and 283,841, 1927; *Brit. Chem. Abs.* **B**, 1929, 485; British Patents 286,272 and 300,167, 1927; *Brit. Chem. Abs.* **B**, 1929, 652; British Patent 294,963, 1928; *Brit. Chem. Abs.* **B**, 1930, 471.

[290] I. G. Farbenindustrie A.-G., British Patents 307,937 and 307,938, 1928; *Brit. Chem. Abs.* **B**, 1930, 830.

[291] I. G. Farbenindustrie A.-G., British Patent 312,949, 1928; *Brit. Chem. Abs.* **B**, 1929, 652. *Cf.* British Patent 368,256, 1930; *Chem. Abs.*, 1933, 27, 2339.

[292] I. G. Farbenindustrie A.-G., British Patent 313,188, 1928; *Brit. Chem. Abs.* **B**, 1929, 652.

[293] I. G. Farbenindustrie A.-G., British Patent 315,356, 1929; *Brit. Chem. Abs.* **B**, 1930, 830.

[294] I. G. Farbenindustrie A.-G., British Patent 329,969, 1929; *Brit. Chem. Abs.* **B**, 1930, 781.

[295] I. G. Farbenindustrie A.-G., British Patent 330,922, 1929; *Brit. Chem. Abs.* **B**, 1930, 830.

[296] I. G. Farbenindustrie A.-G., British Patent 331,265, 1929; *Brit. Chem. Abs.* **B**, 1930, 939.

[297] British Patent 312,741, 1928; *Brit. Chem. Abs.* **B**, 1929, 652.

On oxidizing petroleum or its residues with sodium peroxide, or for several days with nitric acid, it separates into two layers. Kleiber and Gilardi[299] found one layer to be composed of octanaphthenes, which on treatment with sulphur were transformed to xylenes, whereas the other, a turbid aqueous layer, was converted by oxidation with fuming HNO_3 to cyclohexanes first, and then to adipic acid. The xylenes also are oxidized to adipic acid. Terpenes can then be added and, after heating to about 150° C., isoprene and butadiene are formed. From these, artificial rubber can be obtained.

In a process described by Hultman[300] for the partial polymerization of a mineral oil material, such as "Dubbs pressure distillate," topped Californian crude, or similar oil or fraction, oxides of cerium or tin at a temperature of about 95° C. are used. The products are cooled and treated with carbon monoxide or methane in the presence of nickel, palladium or other catalysts at about 32° C., and then with a halogenating agent such as chlorine, bromine, or boron fluoride. A soft, rubbery product is formed, which is separated from the oily material. The distillation of shale and treatment of the condensate to obtain a crude rubber-like material suitable for admixture with rubber has been considered by Camberu, Langstaff and Stapelfeld.[301]

By passing ethylene or its homologues through a heated mixture of acetone or its homologues with fuming sulphuric acid, Stern[302] also obtained rubber-like substances.

Alkali metals in the presence of a limited amount of water have been suggested as catalysts in the production of synthetic rubber from diolefins.[303] The water is added as water of crystallization, using salts such as hydrated calcium chloride, sodium carbonate, sodium sulphate, or magnesium sulphate. Polymerization of diolefins with alkali or alkaline earth metals in the presence of hydrogen and in the absence of organic oxygen compounds has also been described.[304] Nitrogen, carbon dioxide or other inert gases may be present.

Rubber latex mixtures have been prepared by polymerization of emulsions of vegetable oils, fats, or their derivatives, and unsaturated hydrocarbons in the presence of oxygen or oxygen-splitting compounds.[305] For example, butadiene and oleic acid emulsified in water with turkey-red oil are polymerized with benzoyl peroxide at 60° C.

Vinylcyclohexenes and other oily polymers have been obtained by the polymerization of butadiene and its homologues by heat at about 400° C. in the presence of iron, aluminum, copper, nickel or silica gel as catalysts.[306] Eisele and

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[298] *Cf.* Dubosc, Sealed Noté 1012, 1912; *Bull. soc. ind. Rouen,* 1926, **54**, 220; *Chem. Abs.,* 1927, **21**, 673.

[299] French Patent 651,824, 1928; *Chem. Abs.,* 1929, **23**, 3600.

[300] U. S. Patent 1,704,194, Mar. 5, 1929; assigned to Hultman, Duncklee, Monteleone and Simons; *Chem. Abs.,* 1929, **23**, 2071.

[301] French Patent 656,094, 1928; *Chem. Abs.,* 1929, **23**, 4102.

[302] French Patent 477,956, 1914; *Chem. Abs.,* 1916, **10**, 1446; British Patent 297, 1915; *Chem. Abs.,* 1916, **10**, 1717; Swiss Patent 70,285, 1915; *Chem. Abs.,* 1916, **10**, 2417.

[303] I. G. Farbenindustrie A.-G., British Patent 357,488, 1929; *Chem. Abs.,* 1932, **26**, 6183.

[304] I. G. Farbenindustrie A.-G., British Patent 363,810, 1930; *Chem. Abs.,* 1933, **27**, 1784.

[305] I. G. Farbenindustrie A.-G., British Patent 362,845, 1930; *Chem. Abs.,* 1933, **27**, 1535.

[306] I. G. Farbenindustrie A.-G., British Patent 343,116, 1928; *Chem. Abs.,* 1931, **25**, 5435.

Stöhrel[307] have prepared products which can be used in plastics and paints by the polymerization of butadiene or its methyl derivative at 150° to 220° C. under pressure in the presence of a diluent and catalysts such as organic amines or finely divided metals.

Rubber-like plastics have been prepared by polymerizing 2-halogen-1,3-butadienes in the presence of air, oxygen, heat, light, catalysts (benzoyl peroxide, peroxides of sodium, lead or hydrogen, or oxidized turpentine) or under pressure.[308] The polymerization can be controlled by the addition of solvents or inhibitors (phenols, quinones, amines, nitro-compounds, or mercaptans) and the resulting products cured at 50° to 180° C.

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[307] German Patent 539,589, 1928; *Chem. Abs.*, 1932, 26, 2333; British Patent 328,908, 1928; *Brit. Chem. Abs.* B, 1930, 754; German Patent 540,998, 1928; *Chem. Abs.*, 1932, 26, 2333; all patents assigned to I. G. Farbenindustrie A.-G.

[308] E. I. du Pont de Nemours and Co., Inc., British Patents 387,363 and 387,340, 1931; *Brit. Chem. Abs.* B, 1933, 318. See Chapter 27.

Chapter 27

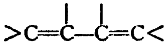
Some Important Reactions of Diolefins

The diolefins are hydrocarbons of the general formula C_nH_{2n-2}, with two ethylene linkages in their molecular structure. They are isomeric with the acetylene series of hydrocarbons. For purposes of classification, the diolefins may be divided into three types which differ in the mutual orientation of the two double bonds and possess somewhat different properties. These three main types are:

(1) The *allenes,* possessing the characteristic structure,

$$>C=C=C<$$

(2) The conjugated dienes (or butadiene type), with the structure,



$$>C=\overset{|}{C}-\overset{|}{C}=C<$$

(3) Other diolefins in which the double bonds are separated from one another by one or more CH_2 groups, among which may be specially mentioned the 1,4- and 1,5-dienes.

Of these three classes the conjugated dienes are by far the most important, both from the point of view of their greater reactivity and power of condensation and because they probably constitute the preponderating diolefin in the products of pyrolysis of hydrocarbons and, therefore, promise to become available commercially in significant quantities.

The gases from both vapor phase and liquid phase cracking processes furnish the principal industrial source of butadiene. For example, Wagner[1] in giving the analysis of a gas from a vapor phase process (Gyro) showed that it contains 1 per cent butadiene. Other analyses of gases from both liquid phase and vapor phase processes indicate that these gases contain from 4.5 to 5.5 per cent collectively of butylenes and butadiene.[2] As the fraction, of which probably about one-seventh is butadiene, can be further separated into butylenes and butadiene by distillation under pressure, the chemical properties and possible utilization of butadiene become of interest to the petroleum technologist.

Flood, Hladky and Edgar[3] pointed out that, of the possible types of unsaturated compounds present in cracked gasolines, the dienes were the most unstable, particularly if the double bonds were not too far apart in the molecule, and that such substances formed gum during storage. The polymerization of the dienes is a well-known phenomenon and part of the sludge formation obtained on treating cracked distillates may be due to the dienes present. From these considerations it is apparent that the chemical properties of the dienes are of importance to the refiner of petroleum products.

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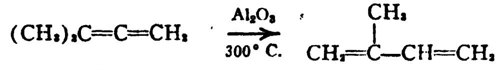
[1] *J. Inst. Pet. Tech.*, 1929, **15**, 484.

[2] Wagner, *Refiner,* 1930, **9** (6), 70; *Chem. Abs.*, 1930, **24**, 5142.

[3] *Ind. Eng. Chem.*, 1933, **25**, 1234. See Kalichevsky and Stagner, "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933, 316.

ALLENES

The allene type of diolefins has not been recognized among the products of pyrolysis. This is probably to be ascribed to the ease with which these hydrocarbons isomerize to the corresponding conjugated diolefins. Thus, unsymmetrical-dimethylallene rearranges to isoprene when passed over alumina at 300° C., especially under diminished pressure.[4] The allenes also isomerize to the corresponding acetylene hydrocarbons when allowed to stand in the presence of metallic sodium, a reaction discovered by Favorsky.[5] These two isomerizations may be represented as follows:



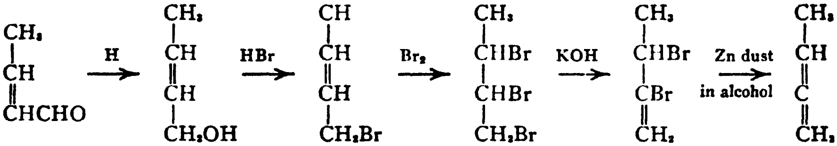
$$(CH_3)_2C{=}C{=}CH_2 \xrightarrow[300^\circ\ C.]{Al_2O_3} CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2$$

unsym.-dimethylallene *isoprene*

$$(CH_3)_2C{=}C{=}CH_2 \xrightarrow{Na} (CH_3)_2CH{-}C{\equiv}CH$$

unsym.-dimethylallene *isopropylacetylene*

The conversion of methylallene into ethylacetylene under the influence of metallic sodium has been described by Jocicz.[6] At high temperatures, however, the reverse reactions occur and the thermal isomerization of methylacetylene to allene at 500° to 650° C. has been observed by Hurd and Meinert.[7] A number of methods are available for the synthesis of the allene hydrocarbons. For laboratory preparation the general method of Bouis[8] seems to possess definite advantages and was the one employed by Hurd and his collaborators in the preparation of pure allene and methylallene. The method is exemplified by the synthesis of methylallene from crotonaldehyde through the following stages:



$$\begin{array}{c}CH_3\\|\\CH\\\|\\CHCHO\end{array} \xrightarrow{H} \begin{array}{c}CH_3\\|\\CH\\\|\\CH\\|\\CH_2OH\end{array} \xrightarrow{HBr} \begin{array}{c}CH\\|\\CH\\\|\\CH\\|\\CH_2Br\end{array} \xrightarrow{Br_2} \begin{array}{c}CH_3\\|\\CHBr\\|\\CHBr\\|\\CH_2Br\end{array} \xrightarrow{KOH} \begin{array}{c}CH_3\\|\\CHBr\\|\\CBr\\\|\\CH_2\end{array} \xrightarrow[\text{in alcohol}]{\text{Zn dust}} \begin{array}{c}CH_3\\|\\CH\\\|\\C\\\|\\CH_2\end{array}$$

In a similar way, allene may be produced by the action of zinc dust on 2,3-dibromo-1-propene, when dissolved in alcohol:[9]

$$CH_2BrCBr{=}CH_2 + Zn \longrightarrow ZnBr_2 + CH_2{=}C{=}CH_2$$

Allene itself is a gas at ordinary temperature (boiling point, —32° C.) and methylallene (1,2-butadiene) is a liquid (boiling point, 19° C.). All the allene hydrocarbons combine readily with bromine (particularly in carbon tetrachloride solution at 0° C.) to yield a dibromide, and ultimately in the presence of excess bromine, to form a tetrabromide. Allene tetrabromide boils at 116° C. at 9 mm. and when pure melts at 10.7° C.[10] Methylallene tetrabromide boils at 97.5° C. at 7 mm. and has a melting point of —2° C.[11]

Subsequently, Bouis[12] developed a general method of making alkylallenes by the action of the appropriate Grignard reagent on acrolein, followed by treatment of the resulting alcohol with phosphorus bromide in pyridine. The pure allyl bromides, $R \cdot CH:CH \cdot CH_2Br$, so formed are brominated at 0° C. to furnish 1,2,3-tribromo-compounds of the type $R \cdot CHBrCHBrCH_2Br$, which are then fused with potash to yield allene dibromides of the formula $RCHBrCBr:CH_2$. Dehalogenation of such dibromides by means of zinc dust and alcohol furnishes the pure allene hydrocarbon. By this series of reactions, Bouis has prepared, *inter alia,* the following allenes: ethylallene, boiling at 45° C.; n-propylallene, boiling at 78° C.; and n-butylallene, boiling at 106° C.

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[4] Webel, U. S. Patent 1,083,164, Dec. 30, 1913; *Chem. Abs.*, 1914, **8**, 830.

[5] *J. Russ. Phys.-Chem. Soc.*, 1887, **19**, 558; *Chem. Soc. Abs.*, 1888, **54**, 1168.

[6] *J. Russ. Phys.-Chem. Soc.*, 1897, **29**, 90; *Chem. Zentr.*, 1897, 1, 1011.

[7] *J.A.C.S.*, 1931, **53**, 289.

[8] *Compt. rend.*, 1926, **182**, 788; *ibid.*, 1926, **183**, 133; *Chem. Abs.*, 1926, **20**, 2145, 3155.

[9] Hurd, Meinert and Spence, *J.A.C.S.*, 1930, **52**, 1138.

[10] Hurd, Meinert and Spence, *J.A.C.S.*, 1930, **52**, 1138; *cf.* Lespieau, *Ann. chim. phys.*, 1897, (7) 11, 252; Gustavson and Demjanov, *J. pr. Chem.*, 1888, (2) **38**, 201.

[11] Hurd and Meinert, *J.A.C.S.*, 1931, **53**, 289; *cf.* Norton and Noyes, *Amer. Chem. J.*, 1888, **10**, 430.

[12] *Ann. chim.*, 1928, (10) **9**, 402.

CONJUGATED DIENES

The conjugated diolefins, notably butadiene, isoprene and 2,3-dimethylbutadiene, have been the object of considerable study, almost entirely, however, from the viewpoint of the production of synthetic rubber. A number of methods of manufacture and synthesis, starting with such abundant raw materials as ethanol, acetone, butanol, fusel oil, and phenol has been worked out but, at present, the synthesis of rubber-like materials from such products, though readily realizable in the laboratory, is still economically impracticable (See Chapter 26). The recognition that the simple diolefins (butadiene and isoprene) are present in not inconsiderable quantities in the products of the pyrolysis of oils and petroleum gases, has again stimulated interest in these substances. The application of the diolefin hydrocarbons in the immediate future seems to be in their conversion into chemical products of the type of solvents and perfumes and similar substances, or in the manufacture of synthetic resins. The conjugated diolefins possess high chemical reactivity so that the difficulties reside not in effecting their combination with other materials but rather in controlling such changes. There is no doubt whatever that when the whole chemistry of the addition reactions of the diolefins, a much neglected subject in aliphatic chemistry, has been well explored, many uses in the synthesis of new and valuable industrial organic products will be discovered.

The production of conjugated diolefins by pyrolysis has already been discussed in some detail (Chapter 4) so that only a brief description of other processes of manufacture is necessary at this point.

BUTADIENE

Besides being a constituent of vapor phase cracking gas, butadiene also occurs in the pressure condensate of coal carbonization gases and in the products of pyrolysis of many organic compounds, notably of cyclohexane, butanol,[13] the lower aliphatic alcohols,[14] fusel oil,[15] and of many dichlorinated products.[16]

Butadiene may also be formed by the elimination of two molecules of hydrogen bromide under the influence of hot soda-lime, from the dibromide of 2-butene:

$$CH_3CH{=}CHCH_3 \text{ (from sec.-butyl alcohol)}$$

$$\Big\downarrow Br_2$$

$$CH_3CHBrCHBrCH_3$$

$$\Big\downarrow \text{soda lime}$$

$$CH_2{=}CHCH{=}CH_2 + 2HBr$$

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[13] Perkin and Matthews, British Patent 17,235, 1912; *J.S.C.I.*, 1913, 32, 884.

[14] Lebedev, British Patent 331,482, 1929; *Brit. Chem. Abs.* B, 1930, 939.

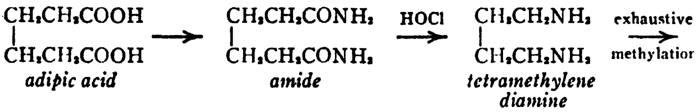
[15] Caventou, *Ann.*, 1863, 127, 93; *Compt. rend.*, 1863, 56, 646, 712.

[16] See Chapter 34 for pyrolysis of chlorinated hydrocarbons.

In the original method, due to Harries,[17] 2,3-dibromobutane was dropped onto soda-lime contained in an iron pot at 600° C. The product thus prepared is not pure and it is necessary to purify it through its tetrabromide, which can be converted to butadiene by zinc and alcohol by the method of Thiele.[18] Jacobson [19] employed a tube furnace and found that better results and less charring were obtained by heating the soda-lime to 530° to 550° C. instead of 600° C. If crotonyl (crotyl) bromide is used as a starting material instead of 2,3-dibromobutane, better yields of butadiene are obtained at lower temperatures (400° to 550° C.).

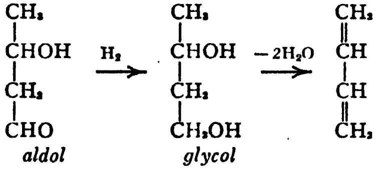
n-Butanol is the starting point of a synthesis of 1,4-butadiene originally suggested by Perkin [20] and later developed as a convenient laboratory method of preparation by Muskat and Northrup.[21] Butanol is converted into its chloride which is chlorinated to yield a mixture of dichlorobutanes. Decomposition of the latter by soda-lime at high temperatures furnishes butadiene. The best yield (about 30 per cent) is obtained in this last stage by passing the 1,4-dichlorobutane fraction over soda-lime at 700° to 730° C.

Another synthesis of butadiene starts with phenol. This is reduced by the Sabatier method to hexahydrophenol which can be oxidized readily (with nitric acid) to adipic acid.[22] Treatment of the amide of this acid with hypochlorite furnishes the diamine and exhaustive methylation of the latter then yields finally, butadiene: [23]



$$\begin{array}{c}CH_2CH_2COOH\\|\\CH_2CH_2COOH\\\textit{adipic acid}\end{array}\longrightarrow\begin{array}{c}CH_2CH_2CONH_2\\|\\CH_2CH_2CONH_2\\\textit{amide}\end{array}\xrightarrow{HOCl}\begin{array}{c}CH_2CH_2NH_2\\|\\CH_2CH_2NH_2\\\textit{tetramethylene}\\\textit{diamine}\end{array}\xrightarrow[\text{methylatior}]{\text{exhaustive}}\begin{array}{c}CH{=}CH_2\\|\\CH{=}CH_2\end{array}$$

One interesting synthesis of butadiene is that in which acetaldehyde (or ethanol) is employed as the raw material. Treatment with dilute alkali converts acetaldehyde into aldol, which may be hydrogenated to 1,3-butylene glycol.[24] Dehydration of this glycol furnishes a good yield of butadiene, thus: [25]



$$\begin{array}{c}CH_3\\|\\CHOH\\|\\CH_2\\|\\CHO\\\textit{aldol}\end{array}\xrightarrow{H_2}\begin{array}{c}CH_3\\|\\CHOH\\|\\CH_2\\|\\CH_2OH\\\textit{glycol}\end{array}\xrightarrow{-2H_2O}\begin{array}{c}CH_2\\\|\\CH\\|\\CH\\\|\\CH_2\end{array}$$

Very good yields of butadiene are obtained by passing 1,3-butylene glycol together with steam over certain dehydrating catalysts. By conducting 80 per cent glycol and 20 per cent steam (at a rate of 100 grams per hour per litre of catalyst) at 270° C. over a catalyst of primary sodium phosphate a yield of 85 to 90 per cent of butadiene is said to result.[26] A dehydration catalyst consisting of phosphoric acid on pumice in conjunction with a pressure of 2 to 20 atmospheres at 250° to 400° C. has been suggested by Mueller-Cunradi and Ober.[26a]

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[17] *Ann.*, 1911, **383**, 176, 181.

[18] Thiele, *Ann.*, 1899, **308**, 333; Birch, *Ind. Eng. Chem.*, 1928, **20**, 474; Farmer, Lawrence and Thorpe, *J.C.S.*, 1928, 729.

[19] *J.A.C.S.*, 1932, **54**, 1545.

[20] *J.S.C.I.*, 1912, **31**, 616.

[21] *J.A.C.S.*, 1930, **52**, 4050.

[22] Bouveault and Locquin, *Bull. soc. chim.*, 1908, (4) **3**, 437; *Chem. Abs.*, 1908, **2**, 1821.

[23] Harries, *Ann.*, 1911, **383**, 179; *Chem. Abs.*, 1911, **5**, 3519.

[24] According to I. G. Farbenindustie A.-G. (British Patent 328,083, 1929) the reduction of aqueous aldol to 1,3-butylene glycol can readily be effected in the presence of reduced copper on silicic acid by hydrogen at 40°-90° C. and 50 to 200 atmospheres pressure.

[25] Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, 1916, **47**, 1947; *J.S.C.I.*, 1916, **35**, 369. German Patent 314,364, 1914; *J.S.C.I.*, 1920, **39**, 83A. Kyriakides, *J.A.C.S.*, 1914, **36**, 980; see Chapter 4.

Other catalysts, such as an oxide or borate with or without activators (copper sulphate or red phosphorus) have also been proposed for this purpose.[27]

A process of Ostromislensky and Kelbasinsky,[28] in which a mixture of acetaldehyde and ethanol is passed first over heated copper and then over heated alumina, probably involves the intermediate formation of aldol, and butylene glycol.

The production of butadiene by passing vinyl bromide through a bath of molten tin has been described by Leyes.[29] The reaction can, presumably, be expressed by the following:

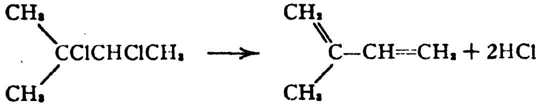
$$2CH_2{=}CHBr + Sn \longrightarrow CH_2{=}CHCH{=}CH_2 + SnBr_2$$

Lebedev [30] suggested the preparation of butadiene by dehydration of the lower aliphatic alcohols over heated catalysts. Butadiene is said to be obtained by passing 95 per cent ethanol over a mixture of aluminum and zinc oxides at 400° C., under a pressure of 0.25 atmospheres. Here again the reaction probably proceeds through the intermediate formation of aldol and butylene glycol.

It is of interest that butadiene was also obtained in a pure condition by the exhaustive methylation of pyrrolidine.[31]

ISOPRENE

Isoprene can be obtained by the pyrolysis of a large number of organic substances, including petroleum oils, rubber, and especially of turpentine.[32] It may be produced, in a manner analogous to the preparation of butadiene, from methyl cyclohexanol (by hydrogenation of cresol). A number of syntheses depend upon the removal of two molecules of hydrogen chloride from the dichloride of trimethylethylene, thus:



$$(CH_3)_2CClCHClCH_3 \longrightarrow (CH_3)(CH_2{=})C{-}CH{=}CH_2 + 2HCl$$

The trimethylethylene necessary for this synthesis may be produced by pyrolysis of monochlorinated pentanes in the presence of barium chloride at 300° to 450° C.[33] or by high temperature dehydration of amyl alcohols. Under these conditions the other amylenes, initially formed, undergo rearrangement to the more stable trimethylethylene.

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[26] Reppe and Hoffmann, U. S. Patent 1,841,055, Jan. 12, 1932; *Chem. Abs.*, 1932, **26**, 1615; British Patent 317,500, 1928; *Brit. Chem. Abs.* **B**, 1929, 886; British Patent 342,411, 1929; *Brit. Chem. Abs.* **B**, 1931, 475; all patents assigned to I. G. Farbenindustrie A.-G.

[26a] U. S. Patent 1,923,569, Aug. 22, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 5082.

[27] I. G. Farbenindustrie A.-G., British Patent 329,396, 1929; *Brit. Chem. Abs.* **B**, 1930, 807.

[28] *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1509; *Chem. Soc. Abs.*, 1916, **110** (1), 5; *J.S.C.I.*, 1916, **35**, 70; *Chem. Abs.*, 1916, **10**, 3179.

[29] British Patent 329,748, 1929; *Brit. Chem. Abs.* **B**, 1930, 807.

[30] British Patent 331,482, 1929; *Chem. Abs.*, 1931, **25**, 115.

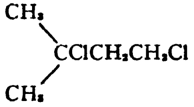
[31] Ciamician and Magnaghi, *Gaz.*, 1885, **15**, 504; *Ber.*, 1885, **18**, 2081.

[32] Hlasiwetz, *Ber.*, 1876, **9**, 1991; Harries, *Ann.*, 1911, **383**, 228; Staudinger and Klever, *Ber.*, 1911, **44**, 2212.

[33] Badische Anilin- und Soda-Fabrik, German Patent 280,596, 1911; *Chem. Abs.*, 1915, **9**, 2164; French Patent 435,312, 1911; *Chem. Abs.*, 1912, **6**, 2548.

Waterman and van Westen[34] employed this method for the preparation of isoprene possessing a theoretical hydrogen absorption value. Amyl alcohol was dehydrated over alumina at 500° C. and the resulting amylene was brominated at —15° C. The vapors of the dibromide were then passed successively over hot barium chloride and then over potassium hydroxide, and the products condensed in liquid air and fractionated. The isoprene thus obtained absorbed 99.6 per cent of the theoretical quantity of hydrogen.

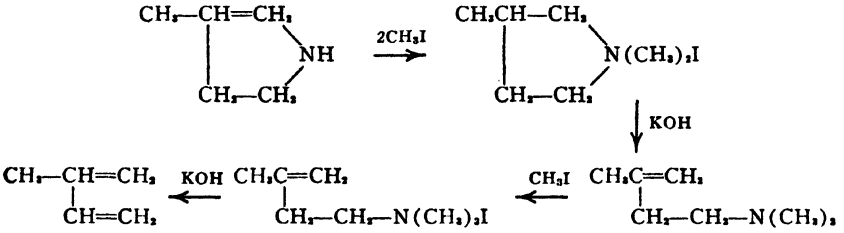
Isoamyl alcohol, the principal constituent of fusel oil, may be used as starting material in the synthesis of isoprene. Chlorination of isoamyl chloride (produced by the action of dry hydrogen chloride on the alcohol) results in the formation of three dichloroisopentanes of which the compound



(boiling point, 15.2° C.)

is the chief product. However, the mixture of isomeric dichlorides may be used for the production of isoprene, the yield being 40 per cent of the theoretical.[35]

Another preparation of isoprene is based upon the exhaustive methylation of methylpyrrolidine,[36] though the process is of no industrial importance. The reactions may be summarized as follows:



The isoprene obtained by many of these processes is always contaminated by impurities. In order to obtain the pure compound it is usually necessary to convert the isoprene into some derivative which can be readily purified and from which the isoprene can be regenerated, e.g., the tetrabromide or sulphone. Farmer and Warren[37] made use of the tertiary alcohol (the so-called "isoprene alcohol") for this purpose. Treatment of crude isoprene at —20° C. with one molecule of pure hydrobromic acid furnishes the 4-bromo-2-methyl-2-butene which can be readily purified by fractionation. This monohydrobromide is converted by the action of 5 per cent aqueous potassium carbonate solution into "isoprene alcohol", or 2-methyl-4-butene-2-ol[38] which can be catalytically dehydrated, by refluxing with aniline hydrobromide and a trace of hydrobromic acid, to yield pure isoprene.[39] The production of isoprene alcohol from the 1,4-hydrobromide of isoprene is an example of simultaneous hydrolysis and isomerization. The process can be summarized in the following manner:

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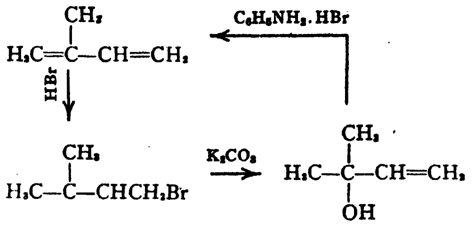
[34] *Rec. trav. chim.*, 1929, **84**, 1084; *Chem. Abs.*, 1930, **24**, 824.
[35] Perkin, *J.S.C.I.*, 1912, **31**, 616.
[36] Euler, *J. pr. Chem.*, 1898, **57**, 132; *Chem. Soc. Abs.*, 1898, **74** (1), 347.
[37] *J.C.S.*, 1931, 3221.
[38] Mokiewski, *J. Russ. Phys.-Chem. Soc.*, 1900, **32**, 207; *Chem. Zentr.*, 1900, **2**, 331.
[39] Kyriakides, *J.A.C.S.*, 1914, **36**, 994.

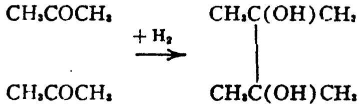


$$\begin{tikzcd} H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \arrow[d, "HBr"'] & \arrow[l, "C_6H_5NH_2.HBr"'] \\ H_3C{-}\overset{CH_3}{\overset{|}{C}}{-}CHCH_2Br \arrow[r, "K_2CO_3"] & H_3C{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH{=}CH_2 \arrow[u] \end{tikzcd}$$

A laboratory method of preparing chemically, pure isoprene from 3-bromo-2-methyl-1-propene has been described by Merejkowsky.[40]

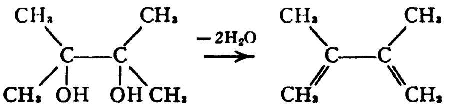
HIGHER DIOLEFINS

The preparation of 2,3-dimethylbutadiene was carried out in Germany during the War, the starting material being acetone. On reduction of acetone by alkaline reagents, particularly amalgams[41] both condensation and reduction occur and the product is pinacone:



$$\begin{array}{c} CH_3COCH_3 \\ \\ CH_3COCH_3 \end{array} \xrightarrow{+H_2} \begin{array}{c} CH_3C(OH)CH_3 \\ | \\ CH_3C(OH)CH_3 \end{array}$$

Pinacone can be dehydrated smoothly in the presence of alumina at about 400° C. to give a good yield of 2,3-dimethylbutadiene.[42] The reaction may be represented as follows:



The production of dimethylbutadiene by the action of heated bases, such as dimethylaniline, on pinacone chlorohydrin[43] and also by the elimination of hydrogen chloride from tetramethylethylene dichloride[44] have also been suggested.

Piperylene (1-methyl-1,3-butadiene or 1,3-pentadiene) may be produced by the dehydration of 2-pentene-4-ol over alumina or kaolin[45] at 400° C. This unsaturated alcohol is formed by the methylation of crotonaldehyde[46] (with methyl magnesium iodide) which in turn can be synthesized from acetaldehyde:[47]

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[40] *Bull. soc. chim*, 1925, 37, 711; *Chem. Abs.*, 1925, 19, 2930.

[41] Holleman, *Rec. trav. chim.*, 1906, 25. 206; *Chem. Soc. Abs.*, 1906, 90 (1), 619; *cf.* Couturier and Meunier, *Compt. rend.*, 1905, 140, 721; *Chem. Soc. Abs.*, 1905, 88 (1), 326.

[42] Farbenfabriken vorm. F. Bayer and Co., German Patent 250,086, 1911; *Chem. Zentr.*, 1912, 2, 776.

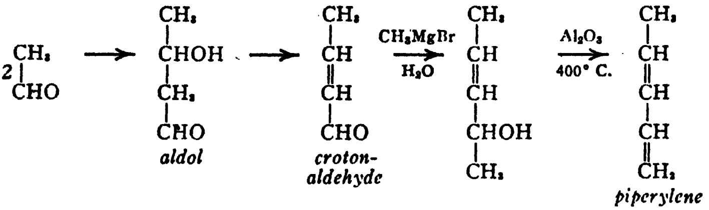
[43] Farbenfabriken vorm. F. Bayer and Co., German Patent 319,505, 1916; *J.S.C.I.*, 1920, 39, 558A.

[44] Kondakow, *J. pr. Chem.*, 1900, (2) 62, 169; *ibid.*, 1901, (2) 63, 113; *Chem. Soc. Abs.*, 1901, 80 (1). 62, 305.

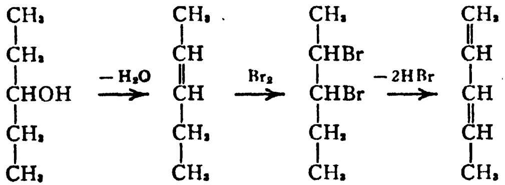
[45] Lebedev, British Patent 331,482, 1929; *Brit. Chem. Abs.* B, 1930, 939; Reif (*Ber.*, 1908, 41, 2744) uses potassium bisulphate for the dehydration.

[46] Grignard, *Ann. de l'Université de Lyon*, 1901, 6, 1; *Chem. Zentr.*, 1901, 2, 622; *Chem. Soc. Abs.*, 1901, 80 (1), 679.

[47] Seyewetz and Bardin, *Compt. rend.*, 1905, 141, 259; *Chem. Soc. Abs.*, 1905, 88 (1), 683; Grignard and Reif, *Bull. soc. chim.*, 1907, (4) 1, 114; *Chem. Soc. Abs.*, 1907, 92 (1), 287.



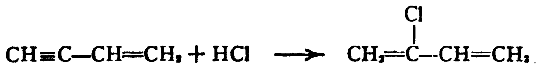
A convenient laboratory method[48] for the preparation of piperylene consists in dehydrating diethylcarbinol[49] with a 50 per cent aqueous solution of sulphuric acid at 100° C. to yield 2-pentene, which is brominated at —20° C. in hexane solution to furnish the dibromide (boiling point, 178° C.). The dibromide loses two molecules of hydrogen bromide to yield piperylene when passed through soda-lime at 500° C.:



Of the cyclic conjugated dienes, cyclopentadiene is of interest since it is one of the products of high temperature pyrolysis of hydrocarbons[50] and has been isolated from the forerunnings of crude benzol (from coal carbonization[51]). 1,3-Cyclohexadiene may be produced by the decomposition of cyclohexene dihalides.[52]

2-CHLOROBUTADIENE

The 2-chloro-derivative of butadiene is obtained by the direct combination of vinylacetylene and concentrated hydrochloric acid in the presence of a mixture of cuprous chloride and ammonium chloride.[53] The addition reaction occurs according to the equation:



$$CH{\equiv}C{-}CH{=}CH_2 + HCl \longrightarrow CH_2{=}\overset{\overset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2$$

This substance, also called chloroprene in order to show its analogy in structure and in chemical behavior to isoprene, is a colorless liquid with an ethereal odor somewhat resembling ethyl bromide and possesses a boiling point of 59.4° C. at 760 mm. and has a specific gravity of 0.9583 at 20° C.

The action of aqueous hydrochloric acid on vinylacetylene results intially in 1,4 addition, the product being 4-chloro-1,2-butadiene. This readily isomerizes to chloroprene.[54] With cuprous chloride present in the reaction mixture the isomerization is much more rapid and no 4-chloro-1,2-butadiene appears to be formed. Larger proportions of hydrochloric acid in the mixture cause the reaction to yield 2,4-dichloro-2-butene.

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[48] Farmer and Warren, *J.C.S.*, 1931, 3221.

[49] This secondary amyl alcohol is being manufactured commercially from pentane.

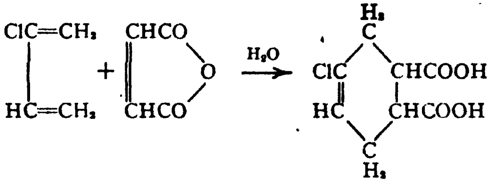
[50] Etard and Lambert, *Compt. rend.*, 1891, 112, 945; *Chem. Soc. Abs.*, 1891, 60, 1085.

[51] Kraemer and Spilker, *Ber.*, 1896, 29, 552.

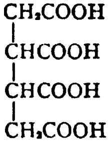
[52] Crossley, *J.C.S.*, 1904, 85, 1410.

[53] Carothers, Williams, Collins and Kirby, *J.A.C.S.*, 1931, 53, 4203. The production of vinylacetylene by the polymerization of acetylene in the presence of hydrochloric acid and cuprous chloride is described by Nieuwland, Calcott, Downing and Carter, *J.A.C.S.*, 1931, 53, 4197; see also Chapter 28.

The chlorine atom in chloroprene is very firmly bound, for only traces of the chloride ion appear on boiling it with alcoholic silver nitrate, alcoholic sodium hydroxide, or pyridine. It reacts with maleic anhydride and yields, after hydrolysis, a white crystalline product which is apparently 4-chloro-1,2,5,6-tetrahydrophthalic acid.



The chlorine atom in this chlorohydrophthalic acid is very firmly bound, being also resistant to the action of boiling alkalies. Oxidation of this compound with boiling nitric acid, however, yields butane-1,2,3,4-tetracarboxylic acid:



$$\begin{array}{l} CH_2COOH \\ | \\ CHCOOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{array}$$

Perhaps the most interesting derivatives of chloroprene, however, are its polymerization products. When allowed to stand for about 10 days in a closed vessel containing a little air, chloroprene changes into a transparent, resilient, non-plastic, elastic mass resembling vulcanized rubber. This product is designated μ-polychloroprene. It has a density of about 1.23 at 20° C., tensile strength of about 140 kg. per sq. cm., and an elongation at break of about 800 per cent. It swells strongly, but does not dissolve in carbon tetrachloride, carbon disulphide, benzene and other organic solvents. Its tendency to imbibe gasoline or lubricating oil is very slight compared with that of natural rubber.[54a]

The polymer formed during the early stages of the reaction just described, which can be isolated by precipitation with alcohol or by distilling off the unchanged chloroprene, is designated α-polychloroprene. Unlike μ-polychloroprene, it is soft, plastic, completely soluble in benzene, and resembles unvulcanized rubber. On standing it is transformed into the μ-polychloroprene.

Aqueous emulsions of chloroprene can be transformed into a polymer resembling μ-polychloroprene and the resulting product which remains suspended constitutes a synthetic latex. The size of the particles is smaller than those of natural latex, hence the particles penetrate porous material more readily. Other polymers which have been isolated are a volatile (β-) polymer, a granular (ω-) polymer, and a balata-like polymer. The rubber-like product is known as

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[54] Carothers, Berchet, and Collins, *J.A.C.S.*, 1932, 54, 4066. E. I. du Pont de Nemours and Co., Inc., French Patent 721,532, 1931; *Chem. Abs.*, 1932, 26, 4061.

[54a] See Bridgwater (*Ind. Eng. Chem.*, 1934, 26, 33) for a comparison of the physical properties of compositions made from polymerized chloroprene (DuPrene) and rubber, respectively.

DuPrene and a plant for producing it by the polymerization of chloroprene has been constructed by E. I. duPont de Nemours & Co., Inc., at Deepwater, N. J.[55]

PROPERTIES OF CONJUGATED DIENES

Table 115 summarizes the data on the physical constants of the simpler acyclic and monocyclic conjugated diolefins:

TABLE 115.—*Physical Constants of Conjugated Diolefins.*

Name	Boiling Point	Density	Refractive Index n_D^{20}
1,3-Butadiene	−5° C.,[a] −4° C.,[b] −2.6° C.[k]	—	—
2-Methyl-1,3-butadiene (Isoprene)	33.9°–34.0° C.[c] 34.5°–35.0° C.[d] [e]	d_0^{19} 0.6794[e] d_4^{20} 0.6806[e]	1.4262[e] 1.4194[e]
1-Methyl-1,3-butadiene (Piperylene)	42° C.[f]	d_0^{0} 0.6952[g] d_4^{25} 0.6794[h]	1.4206[h]
2,3-Dimethyl-1,3-butadiene	69.5° C.[i]	d_0^{0} 0.7446[i] d_{20}^{20} 0.7273[i]	1.4377[i]
2,4-Hexadiene	80°–82° C.[h]	d_4^{21} 0.7177[h]	1.4463 at 21° C.[h]
Cyclopentadiene	41° C.[j]	d_{15}^{15} 0.815[j]	—

[a] Thiele, *Ann.*, 1899, **308**, 337.
[b] Grimaux and Cloez, *Bull. soc. chim.*, 1887, (2) **48**, 31.
[c] Harries, *Ber.*, 1914, **47**, 1999.
[d] Lebedev, *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1249; *Chem. Soc. Abs.*, 1913, **104** (1) 1288.
[e] Waterman and van Westen, *Rec. trav. chim.*, 1929, **84**, 1084.
[f] Hofmann, *Ber.*, 1881, **14**, 665.
[g] Wosnesenski, *J. Russ. Phys.-Chem. Soc.*, 1904, **36**, 532; *Chem. Zentr.*, 1904, **2**, 183.
[h] Reif, *Ber.*, 1908, **41**, 2744.
[i] Kondakow, *J. pr. Chem.*, 1900, (2) **62**, 172.
[j] Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436.
[k] "International Critical Tables," National Research Council, McGraw-Hill Book Co., New York, 1926, **1**.

The simple conjugated diolefins are highly refractive, easily volatile liquids having a pungent odor. Many of them are unstable, and, on standing in the presence of air or sunlight, tend to undergo polymerization and autoxidation. On a laboratory scale, they can usually be separated from a mixture with other hydrocarbons by conversion into their tetrabromides which, in most cases, are readily crystallizable solids. Their tetrabromides are reducible to the parent diolefin by the zinc-copper couple of Gladstone and Tribe.[56] Various methods have been proposed for the separation of diolefins from other hydrocarbons. Among these may be mentioned the following: selective solution in certain organic solvents, such as ethylene glycol mono- or di-acetates, furfural, or bases such as aniline;[57] and absorption in aqueous solutions of certain salts of the metals of Groups I and II of the periodic system. Monolefins are also absorbed by such solutions but advantage may be taken of the fact that diolefins and the salts form precipitates which can be separated by filtration. Thus, with solutions of cuprous chloride, butadiene gives a solid double compound which is precipitated from the solution, whereas the double compounds of the monolefins remain in solution.[58] The diolefins may be recovered from such double compounds by heating or by reducing the pressure. A material which can be used for separating conjugated diolefins from mixtures is anhydrous sulphur dioxide, which readily combines with such hydrocarbons in the presence of a small proportion of a phenol, amine, or copper salt to furnish monomeric sulphones. The latter are resolved into their parent materials by heating to temperatures of about 120° C.[59] Butadiene may be separated from its mixture with more reactive monolefins (such as isobutylene) by taking advantage of the fact that the butadiene is less readily absorbed by sulphuric acid than these monolefins.[60] The separation of substantially pure butadiene from a liquid mixture containing butylene by distillation at about 45° C. under 5 atmospheres pressure has also been effected.[61] Since many materials favor the polymerization of diolefins, the distillation of these hydrocarbons on a large scale demands equipment constructed of non-catalytic metals. For distilling butadiene hydrocarbons under pressure the use of plant constructed of magnesium, copper, manganese, zinc, tin, cadmium, cobalt, nickel, lead, aluminum, precious metals or stainless steel alloys has been recommended.[62]

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[55] *Ind. Eng. Chem., News Ed.,* Nov. 10, 1931. The production of synthetic rubber by the polymerization of butadiene hydrocarbons has already been discussed in Chapter 26. Other polymerizations of acetylene hydrocarbons are mentioned in Chapter 28. See also Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York. For a discussion of the problem of the production of synthetic rubber, see Carothers, *Ind. Eng. Chem.*, 1934, **26**, 30.

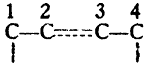
[56] *Proc. Royal Soc.*, 1872, **20**, 218; *J.C.S.*, 1872, **25**, 461. See also *J.C.S.*, 1873, **26**, 445.

[57] I. G. Farbenindustrie A.-G., British Patent 319.025, 1928; *Brit. Chem. Abs.* **B**, 1930, 50.

All the conjugated dienes exhibit a high chemical reactivity which renders them capable of undergoing a large number of addition reactions with all kinds of chemical reagents. However, diolefins with a conjugated system of double bonds behave in a peculiar manner on addition of two atoms of a univalent atom or group of atoms. It might be expected, for example, that butadiene would combine with two bromine atoms to yield the 1,2-dibromide exclusively, thus:

$$CH_2Br.CHBr.CH{=}CH_2$$

As a matter of fact, however, it is the 1,4-dibromide which is produced to a preponderating extent. To explain the formation of 1,4 addition products of conjugated diolefins, Thiele[63] assumed that the whole of the affinity of the double bond is not employed but that a part, called the "residual affinity", remains free at atoms 1 and 4, the remainder being satisfied between atoms 2 and 3. Thiele's conception of the valency distribution in conjugated systems may be represented by the scheme:



$$\begin{array}{cccc}1&2&3&4\\ C-&C\overset{\cdots\cdots}{=\!=}&C-&C\\ \vdots&&&\vdots\end{array}$$

in which the dotted lines denote partial valencies.

There is thus established a partial double bond between carbon atoms 2 and 3, but this is less active than the "residual affinities" on carbon atoms 1 and 4. When butadiene reacts with bromine the 1,4 addition product is first formed, thus satisfying the "residual affinities" and establishing a double bond between carbon atoms 2 and 3. In the presence of an excess of bromine the tetra- addition product having a normal structure is formed.

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[58] Feiler, British Patent 303,323, 1928; *Brit. Chem. Abs.* **B**, 1929, 199; U. S. Patent 1,795,549, March 10, 1931; *Chem. Abs.*, 1931, **25**, 2435; both patents assigned to I. G. Farbenindustrie A.-G. Bataafsche Petroleum Maatschappij, British Patent 359,234, 1930; *Brit. Chem. Abs.* **B**, 1932, 9.

[59] Staudinger, French Patent 698,857, 1930; *Chem. Abs.*, 1931, **25**, 3360.

[60] I. G. Farbenindustrie A.-G., French Patent 703,743, 1930; *Chem. Abs.*, 1931, **25**, 4555.

[61] Schmidt and Grosskinsky, U. S. Patent 1,832,428, Nov. 17, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 1302. See also Chapter 4.

[62] I. G. Farbenindustrie A.-G., French Patent 699,910, 1930; *Chem. Abs.*, 1931, **25**, 3357.

[63] *Ann.*, 1899, **306**, 87; *Chem. Soc. Abs.*, 1899, **76** (1), 554.

The impression has prevailed that all conjugated diolefins furnish 1,4 addition compounds exclusively. This is by no means the case, however, for it has been shown that the addition of two atoms of bromine to the simple conjugated diolefins results in the formation of both 1,4 and 1,2 addition compounds, though the latter are usually formed to a much less extent. The proportion of the two isomers formed depends greatly upon the solvent employed, higher proportions of 1,2-addition products being formed in non-polar solvents than in polar or readily polarizable solvents.[64] Constitutional influences also exert an effect on the proportion of the two isomers formed and 1-phenylbutadiene appears to yield 3,4-dibromide almost exclusively, irrespective of conditions.[65]

Though the diolefins resemble the monolefins in their general tendency to form addition products with numerous reagents, the former hydrocarbons are very much more reactive and their power of polymerization much more highly developed. Certain inorganic reagents, which combine smoothly with the simple monolefins to furnish well-defined addition compounds, react with conjugated diolefins with almost explosive violence to form polymers and tarry materials. Thus, for example, concentrated sulphuric acid reacts with many conjugated dienes to form tars with reduction of the acid while more dilute acids tend to form high molecular weight resins. This is particularly true of the action of sulphuric acid on the cyclic 1,3-diolefins such as cyclopentadiene and 1,3-cyclohexadiene. The production of tarry matters in the refining of cracked distillates with sulphuric acid is sometimes ascribed to the presence of conjugated diolefins and similar reactive hydrocarbons. The conjugated diolefins also exhibit a very much greater power of autoxidation and peroxide formation than the monolefins and are probably largely responsible for gum formation in cracked gasolines. (See Chapter 40.)

In the following brief account of the reactions of the simpler conjugated diolefins with various organic and inorganic reagents, an attempt has been made to summarize such reactions as are likely to be of industrial interest either from the viewpoint of the refiner or from that of the chemist. In particular, the great chemical reactivity of the simple butadiene derivatives appears to be the gateway to a wide field of possibilities in the utilization of these abundant hydrocarbons for industrial organic syntheses. In the following account, attention will be concentrated upon butadiene, the simplest and most abundant hydrocarbon of the series.

Although it is desirable to discuss the conjugated diolefins as a single class of hydrocarbons, it must be borne in mind that generalizations about a series cannot take into account the variations among the individual members. It must not be imagined that all the conjugated diolefins possess a similar degree of reactivity either to different or to the same chemical reagents. The conjugated dienes exhibit wide individual variations in their reactivities. In general, the order of diminishing chemical reactivity is: conjugated cyclic diolefins, butadiene homologues, butadiene.

REACTIONS OF CONJUGATED DIOLEFINS WITH BROMINE AND CHLORINE

As previously stated, the addition of halogens to the conjugated dienes proceeds in two stages, first a dihalogen addition product being formed and then, in presence of excess halogen, a tetrahalogen compound. Farmer, Lawrence and Thorpe[66] found that addition of the requisite quantity of bromine to butadiene in chloroform solution at —15° C. resulted in the production of the 1,4-dibromide together with about 37 per cent of the 1,2-product, as indicated:

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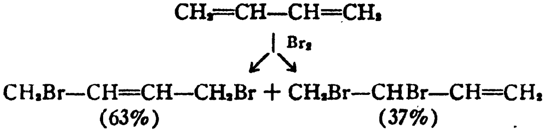
[64] Ingold and Smith, *J.C.S.*, 1931, 2752.

[65] Muskat and Huggins, *J.A.C.S.*, 1929, 51, 2496.



$$\begin{array}{c} CH_2{=}CH{-}CH{=}CH_2 \\ \downarrow Br_2 \\ \underset{(63\%)}{CH_2Br{-}CH{=}CH{-}CH_2Br} + \underset{(37\%)}{CH_2Br{-}CHBr{-}CH{=}CH_2} \end{array}$$

Griner[67] had previously observed that the addition of bromine to a chloroform solution of butadiene (at —21° C.) resulted in the formation of a liquid dibromide. He further found that this dibromide on being heated to 100° C. changed into the solid isomer, melting at 53° to 54° C., which was considered to be the *trans*-1,4-dibromobutadiene. A small quantity of a liquid dibromide which remained, boiling at 70° C. at 2 mm., was considered to be the *cis*-1,4-dibromobutadiene. This *cis* form of the dibromide was not detected by Farmer, Lawrence and Thorpe,[68] and its existence has been contested also by Thiele.[69]

In a similar way the addition of two atoms of chlorine to butadiene in solution results in the formation of both 1,4- and 1,2-products.[70] Combination of butadiene with one molecule of iodine monochloride in methylene dichloride solution at —35° C. results[71] in the production mainly of the 1,4-compound together with about 22 per cent of the 1,2-isomer, $CH_2ICHClCH{=}CH_2$.

Addition of two atoms of bromine to isoprene in chloroform solution at 0° C. yields two isomeric dibromides[72] but, according to Staudinger and his collaborators, the main product is always the 1,4-compound.[73]

Of the other conjugated diolefins, the 2,3-, 1,4-, and 1,3-dimethylbutadienes yield mixtures of dibromides with a preponderating content of the 1,4-product.[74] On the other hand, 1-phenylbutadiene furnishes,[75] under widely different temperature conditions and in different solvents, only the 3,4-dichloride, $C_6H_5CH{=}CH{=}CHCl{-}CH_2Cl$.

Cyclopentadiene forms both 1,2- and 1,4-dibromides, the latter in larger amount. Farmer and Scott[76] stated that the proportion of the 1,4-compound is increased by changing the solvent from hexane to chloroform. The 1,4-dibromide of cyclopentadiene exists in two stereoisomeric forms, one a liquid (b.p., 53° to 54° C. at 2 mm.) and the other a crystalline solid (m.p., 45° to 46° C.).[77] Bromination is conveniently effected in chloroform solution at —10° to —15° C.

The tetrahalides of the conjugated diolefins are readily prepared by adding an excess of halogen to a solution of the diolefins cooled to 0° C. or below. They frequently exist in two stereoisomeric forms. They may be utilized in the purification of diolefins. From the diolefin tetrahalide, the diolefin may be regenerated by reduction with zinc in alcohol.[78] 1,2,3,4-Tetrabromobutane is a typical member of the series of diolefin tetrahalides. It exists in two forms, one melting at 118° C. and boiling at 260° to 270° C., and another melting at 39° C. and boiling at 180° to 181° C., both forms being produced (in approximately equal amount) by the action of excess bromine on butadiene (in carbon tetrachloride solution at 0° C.).[79] Jacobson[80] obtained butadiene tetrabromide by passing a slow stream of crude butadiene through bromine cooled in an ice-bath. The butadiene tetrabromide (melting point, 116° to 117° C.) was contaminated with quantities of other bromobutanes, including 1,1,4,4-tetrabromobutane and the isomeric butadiene tetrabromide (melting point, 38° C.). When treated with sodium ethoxide in cold alcoholic solution butadiene tetrabromide loses two molecules of hydrobromic acid and is converted into 2,3-dibromobutadiene, $CH_2=CBr-CBr=CH_2$, (boiling point, 44° C. at 10 mm., and melting point, —21.5° C.). Heated with excess of alcoholic potash at 150° to 160° C. either of the butadiene tetrabromides gives a small yield of the hydrocarbon, diacetylene, $CH\equiv C-C\equiv CH$, a colorless gas condensible to a liquid (boiling point, 10° C.; d^{5}0.7107; and n, 1.4198).[81]

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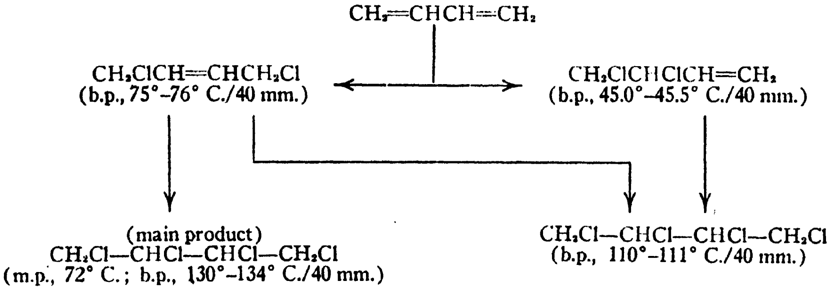
[66] *J.C.S.*, 1928, 729.
[67] Griner, *Compt. rend.*, 1893, **117**, 553; *Chem. Soc. Abs.*, 1894, **66** (1), 62; *Chem. Zentr.*, 1893, **2**, 1085.
[68] *Loc. cit.*
[69] *Ann.*, 1899, **308**, 333; *Chem. Soc. Abs.*, 1900, **78** (1), 2.
[70] Muskat and Northrup, *J.A.C.S.*, 1930, **52**, 4043.
[71] Ingold and Smith, *J.C.S.*, 1931, 2752.
[72] Bergmann, *J. Russ. Phys.-Chem. Soc.*, 1920, **52**, 24; *Chem. Abs.*, 1923, **17**, 1420.
[73] Staudinger, Muntwyler and Kupfer, *Helv. Chim. Acta*, 1922, **5**, 756; *Chem. Abs.*, 1923, **17**, 2974.
[74] Farmer, Lawrence and Scott, *J.C.S.*, 1930, 510.
[75] Muskat and Huggins, *J.A.C.S.*, 1929, **51**, 2496.
[76] *J.C.S.*, 1929, 172.
[77] Thiele, *Ann.*, 1901, **314**, 296; *Chem. Soc. Abs.*, 1901, **80** (1), 181.
[78] Thiele, *Ann.*, 1899, **308**, 339; *Chem. Soc. Abs.*, 1900, **78** (1) 2.

The tetrachlorides of the butadiene hydrocarbons are readily obtained by treatment with chlorine in a solvent. Two stereoisomeric butadiene tetrachlorides result from treatment of butadiene with chlorine in chloroform, carbon disulphide or petroleum solution, one form boiling at 110° to 111° C. at 40 mm., and the other melting at 72° C. and boiling at 130° to 134° C. at 40 mm. The latter variety is the main product of the continued chlorination of 1,4-dichloro-2-butene, whereas the lower-boiling stereoisomer forms on the further addition of chlorine to 3,4-dichloro-1-butene. The chlorine addition reactions of butadiene can accordingly be represented by the scheme:[82]


$CH_2=CHCH=CH_2$
$CH_2ClCH=CHCH_2Cl$
(b.p., 75°-76° C./40 mm.)
$CH_2ClCHClCH=CH_2$
(b.p., 45.0°-45.5° C./40 mm.)
(main product)
$CH_2Cl-CHCl-CHCl-CH_2Cl$
(m.p., 72° C.; b.p., 130°-134° C./40 mm.)
$CH_2Cl-CHCl-CHCl-CH_2Cl$
(b.p., 110°-111° C./40 mm.)

According to Sorokin and Belikov,[83] butadiene tetrachloride (m.p., 70° C.; b.p., 118° to 122° C.), which can be prepared by passing butadiene through carbon tetrachloride saturated with chlorine at 15° to 16° C., may be employed in the estimation of butadiene in mixtures of unsaturated gases. The yield of tetrachloride is said to be within 2.5 to 5.0 per cent of the theoretical.

The tetrahalides of butadiene homologues are very similar to those of butadiene. Piperylene tetrabromide exists in two stereoisomeric forms, a crystalline solid melting at 114.5° C. and a liquid boiling at 115° to 118° C. at 4 mm.[84] Isoprene tetrabromide (b.p., 153° to 155° C. at 12 mm.) on treatment with sodium ethoxide yields a dibromoisoprene, boiling at 78° to 83° C. at 12 mm.[85]

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[79] Ciamician and Magnaghi, *Ber.*, 1885, **18**, 2079; *ibid.*, 1886, **19**, 570; *ibid.*, 1887, **20**, 3064; *ibid.*, 1888, **21**, 1430; Willstätter and von Schmädel, *Ber.*, 1905, **38**, 1997; Willstätter and Bruce, *Ber.*, 1907, **40**, 3987.

[80] *J.A.C.S.*, 1932, **54**, 1545.

[81] Lespieau and Prevost, *Compt. rend.*, 1925, **180**, 675; *Chem. Abs.*, 1925, **19**, 1693.

[82] Muskat and Northrup, *J.A.C.S.*, 1930, **52**, 4043.

[83] *J. Chem. Ind. (Moscow)*, 1925, **1**, 28; *Chem. Abs.*, 1926, **20**, 352.

[84] Magnanimi, *Gazzetta*, 1886, **16**, 391; *Chem. Soc. Abs.*, 1887, **52**, 457.

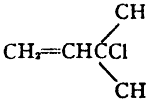
REACTIONS OF CONJUGATED DIOLEFINS WITH HALOGEN ACIDS

Conjugated diolefins combine readily with halogen acids, either anhydrous or in very concentrated solution, to furnish both mono- and di-hydrohalides, the latter being the products obtained in the presence of excess of reagent. These reactions usually proceed very smoothly and without appreciable polymerization. The main result of the addition of one molecule of hydrogen halide to conjugated dienes appears to be always the 1,4-product but certain negatively substituted dienes (such as 1-phenylbutadiene and 1-bromobutadiene) yield only 3,4-addition compounds.

The addition of hydrogen halides to butadiene has apparently been very little studied. Combination of hydrogen bromide with butadiene in glacial acetic acid solution has been said[86] to give an 85 per cent yield of crotonyl (crotyl) bromide:

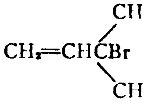
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{HBr} CH_3.CH{=}CH.CH_2Br$$

Somewhat contradictory statements have been made with regard to the addition of one molecule of hydrogen halides to isoprene. According to the earlier investigators both hydrogen chloride[87] and hydrogen bromide[88] combine with the formation of



$CH_2{=}CHC(CH_3)(CH_3)Cl$

and



$CH_2{=}CHC(CH_3)(CH_3)Br$

respectively.

The addition of one molecule of hydrogen bromide to crude isoprene cooled to —20° C. was studied by Claisen, Kremers, Roth and Tietze.[89] They concluded that the initial product of the reaction was the above tertiary bromide, i.e., 3-bromo-3-methyl-1-butene, but that this compound can isomerize under certain conditions to yield the 1,4-addition compound, 2-methyl-4-bromo-2-butene. Addition of hydrogen bromide to ice-cold isoprene with avoidance of excess of hydrogen bromide was found to yield a material boiling largely below 50° C. at 40 mm., particularly if the distillation was carried out immediately after the addition reaction. If, however, the reaction product was not distilled within a few hours, and especially if excess hydrogen bromide was present, it was observed that the reaction product boiled at 50° to 51° C. at 40 mm. and consisted largely of the primary bromide, 2-methyl-4-bromo-2-butene. Staudinger, Kreis and Schilt[90] found that treatment of 100 grams of isoprene in acetic acid solution with 122 grams of bromine for 2 days at 0° C. led to the production of 74 per cent of the 1,4-hydrobromide, $CH_3C(CH_3){=}CHCH_2Br$, the constitution of which was proved by oxidation. A possible explanation of the discrepancy between the results of various workers is that both types of monohydrohalide are formed, the relative proportion of the isomers depending upon the conditions. The monohydrochloride of isoprene, obtained by Aschan[91] by treating isoprene with hydrogen chloride in the presence of a little water in the cold, was a liquid (boiling point, 107° to 110° C. and d^{20}_{4} 0.9335) possessing a smell similar to that of allyl chloride. It was readily oxidized with permanganate and added a second molecule of dry hydrogen chloride with the formation of the dihydrohalide.

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[85] Staudinger, Muntwyler and Kupfer, *Helv. Chim. Acta*, 1922, 5, 756; *Chem. Abs.*, 1923, 17, 2974

[86] Meisenburg, German Patent 522,650, 1927, assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 3672.

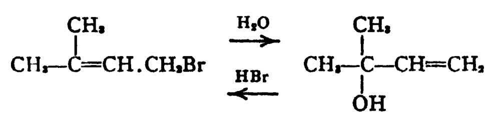
[87] Kondakow, *J. Russ. Phys.-Chem. Soc.*, 1889, 21, 36; *Chem. Zentr.*, 1890, 1, 311.

[88] Mokijewski, *J. Russ. Phys.-Chem. Soc.*, 1900, 32, 207; *Chem. Soc. Abs.*, 1900, 78 (1), 509; Bergmann, *J. Russ. Phys.-Chem. Soc.*, 1930, 52, 24; *Chem. Abs.*, 1923, 17, 1420.

[89] *J. prakt. Chem.*, 1922, (2) 105, 65; *Chem. Soc. Abs.*, 1923, 124 (1), 1050.

[90] *Helv. Chim. Acta*, 1922, 5, 743; *Chem. Abs.*, 1923, 17, 2974.

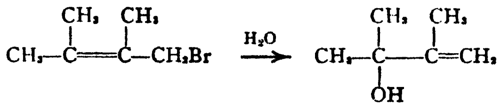
The 1,4-monohydrobromide of isoprene is unusually easily hydrolyzed by water, being converted into a tertiary alcohol, the so-called "isoprene alcohol" of Mokijewski.[92] Although this conversion involves simultaneous hydrolysis and shifting of the double bond, the tertiary alcohol is evidently produced directly and not through the intermediate formation of the corresponding primary alcohol (3-methyl-2-butene-1-ol) since the latter shows no tendency to isomerize.[93] Claisen and his collaborators[94] studied this hydrolysis and concluded that it could be carried to completion by the use of sodium carbonate solution. The reaction is reversible since the isoprene alcohol is converted into the primary bromide by the action of hydrobromic acid, and can, accordingly, be represented as follows:



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH.CH_2Br \underset{HBr}{\overset{H_2O}{\rightleftarrows}} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH=CH_2$$

1,4-hydrobromide *"isoprene alcohol"*

This hydrolytic conversion is also displayed by the 1,4-hydrobromide of 2,3-dimethylbutadiene (the principal product of the action of hydrogen bromide on that hydrocarbon), which is hydrolyzed to a tertiary (and not, as might be expected, a primary) alcohol by the action of aqueous sodium carbonate. The tertiary alcohol, namely 1,1,2-trimethylallyl alcohol, is formed as follows:



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2Br \xrightarrow{H_2O} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

The dihydrohalides of isoprene are readily prepared either from the diene or from its monohydrohalide. Thus, treatment of isoprene with two molecular proportions of hydrogen bromide in glacial acetic acid solution[95] furnishes the dihydrobromide of the constitution $(CH_3)_2CBrCH_2\text{-}CH_2Br$.

The dihydrochloride was obtained by Aschan[96] in 94 per cent yield by treating the monohydrochloride with concentrated hydrochloric acid saturated with dry hydrogen chloride. The reaction proceeded smoothly without polymerization and the product, 2,4-dichloro-2-methylbutane, $(CH_3)_2CCl\text{-}CH_2\text{-}CH_2Cl$, has a boiling point of 52° to 53° C. at 12 mm., 145° to 146° C. at 760 mm. Ostromislensky[97] proposed a method of estimating isoprene in mixtures containing amylenes and butylenes, which consists in converting the isoprene into the above di-hydrochloride by shaking with fuming hydrochloric acid for 6 hours and separating this substance from admixed secondary and tertiary amyl and butyl chlorides by fractionation.

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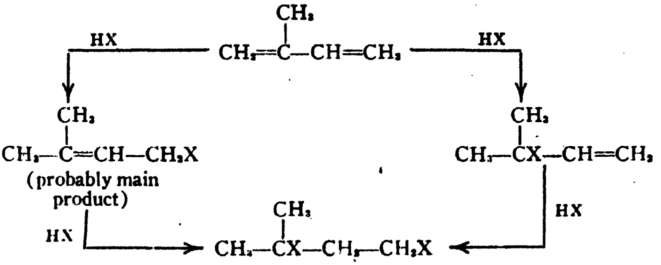
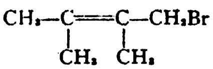
[91] *Ber.*, 1918, 51, 1303.
[92] *J. Russ. Phys.-Chem. Soc.*, 1899, 32, 207; *Chem. Zentr.*, 1900, 2, 331.
[93] Courtot, *Bull. soc. chim.*, 1906, (3) 35, 657; *Chem. Soc. Abs.*, 1906, 90 (1), 788.
[94] Claisen, Kremers, Roth and Tietze, *loc. cit.*
[95] Ipatiev and Wittorf, *J. pr. Chem.*, 1897, (2) 55, 1.
[96] *Loc. cit.*
[97] *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 1978; *Chem. Abs.*, 1916, 10, 1341.

The addition of hydrogen halides to isoprene may be represented as follows:

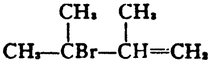


Of the other simple homologues of butadiene, 2,3-dimethylbutadiene adds on hydrogen bromide in two stages and the monohydrobromide consists mainly of the 1,4-compound:[98]



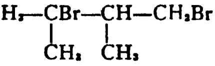
$$CH_3{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_2Br$$

According to Claisen and his collaborators,[99] the main product of the addition of one molecule of hydrogen bromide is the above 1,4-hydrobromide, a lacrimatory oil boiling at 51° to 54° C. at 20 mm., but there is evidence that the tertiary bromide



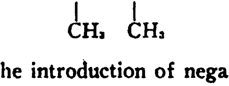
$$CH_3{-}\overset{CH_3}{C}Br{-}\overset{CH_3}{C}H{=}CH_2$$

is formed initially and then undergoes isomerization, since the reaction product has a much lower boiling point (27° to 50° C. under 20 mm.) if distilled immediately after its formation. The dihydrobromide consists of the 2,4-dibromo-compound,



$$CH_3{-}\underset{CH_3}{C}Br{-}\underset{CH_3}{C}H{-}CH_2Br$$

though, according to Bergmann,[100] it is also accompanied by about 30 per cent of the isomeric 2,3-dibromo-compound (described by Thiele[101]) with the structure



$$CH_3{-}\underset{CH_3}{C}Br{-}\underset{CH_3}{C}Br{-}CH_3$$

The marked influence of the introduction of negative groups into the butadiene molecule on the mode of addition of halogens, is well illustrated by the combination of 1-phenylbutadiene[102] and 1-bromobutadiene[103] with hydrogen bromide. In both cases 3,4-addition products are formed in accordance with the scheme:

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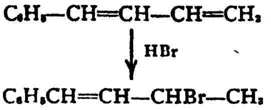
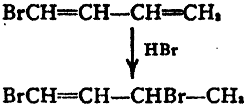
[98] Farmer and Marshall, *J.C.S.*, 1931, 129.
[99] Claisen, Kremers, Roth and Tietze, *loc. cit.*
[100] *J. Russ. Phys.-Chem. Soc.*, 1920, 52, 24; Chem. *Abs.*, 1923, 17, 1420.
[101] *Ber.*, 1894, 27, 454.
[102] Riiber, *Ber.*, 1911, 44, 2977.
[103] Ingold and Smith, *J.C.S.*, 1931, 2752.



$$C_6H_5{-}CH{=}CH{-}CH{=}CH_2 \xrightarrow{HBr} C_6H_5CH{=}CH{-}CHBr{-}CH_3$$

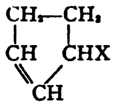


$$BrCH{=}CH{-}CH{=}CH_2 \xrightarrow{HBr} BrCH{=}CH{-}CHBr{-}CH_3$$

Similarly, it was later observed[104] that 2-chlorobutadiene combines readily with aqueous hydrochloric acid in the presence of cuprous chloride as catalyst with the production of 1,3-dichlor-1-butene, thus:

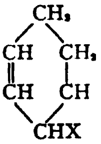
$$CH_2{=}CCl{-}CH{=}CH_2 \xrightarrow{HCl} CH_3{-}CCl{=}CHCH_2Cl$$

The cyclic diolefins, cyclopentadiene[105] and 1,3-cyclohexadiene[106] combine readily with one molecule of hydrogen halide to yield products having the constitutions



(X = halogen atom)

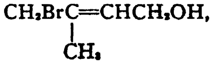
and



The hydrochloride of cyclopentadiene (b.p., 50° C. at 40 mm.) is not further acted upon even by an excess of hydrogen chloride though it combines readily with chlorine to furnish 1,2,3-trichlorocyclopentane (b.p., 196° C.).[105]

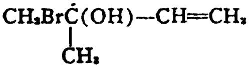
Halohydrins of the Diolefins

With hypochlorous acid or bromine water the conjugated dienes react with the production of both mono- and di-halohydrins. The dichlorohydrin of isoprene was isolated as a crystalline solid melting at 82° C. by Mokijewski.[107] The action of bromine water on isoprene and 1-phenylbutadiene has been shown by Ingold and Smith[108] to yield monobromohydrins of these hydrocarbons. When treated with bromine water in the cold, isoprene gave a mixture of bromohydrins, which was shown to contain about 47 per cent of the compound:



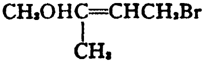
$$CH_2BrC(CH_3){=}CHCH_2OH,$$

about 16 per cent of



$$CH_2BrC(OH)(CH_3){-}CH{=}CH_2$$

together with a small amount of



$$CH_2OHC(CH_3){=}CHCH_2Br$$

Evidently 1,4-addition products also predominate.

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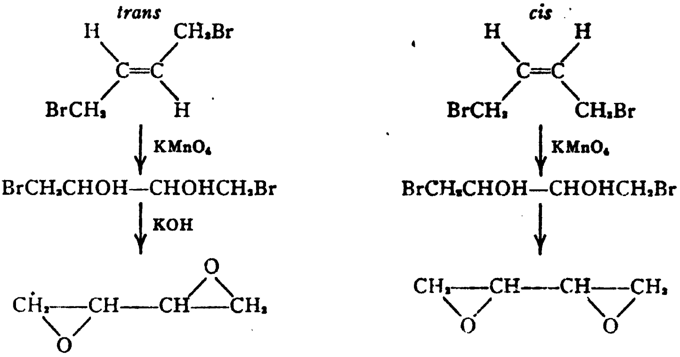
[104] Carothers, Williams, Collins and Kirby, *J.A.C.S.*, 1931, **53**, 4203.
[105] Kraemer and Spilker, *Ber.*, 1896, **29**, 554.
[106] Crossley, *J.C.S.*, 1904, **85**, 1420.
[107] *J. Russ. Phys.-Chem. Soc.*, 1898, **30**, 885; *Chem. Zentr.*, 1899, **1**, 589.
[108] *J.C.S.*, 1931, 2752.

By the action of bromine water on 1-phenylbutadiene an oily monobromohydrin of the structure $C_6H_5CH{=}CHCHOHCH_2Br$ was obtained, further illustrating the effect of negative groupings on the orientation of addition compounds.

Griner[109] reported obtaining two stereoisomeric butadiene dibromohydrins by mild oxidation with 1 per cent potassium permanganate solution of the cis and trans forms of butadiene 1,4-dibromide. The action of anhydrous caustic alkali converts these bromohydrins into two stereoisomeric oxides. The reactions may be summarized as follows:



m.p., 4° C.; b.p., 59°-60° C. at 30 mm. m.p., −15° C.; b.p., 49° C. at 20 mm.

Reaction of Conjugated Diolefins with Sulphuric Acid

The conjugated dienes exhibit wide variations in their behavior towards sulphuric acid. The more reactive members such as the cyclic dienes, cyclopentadiene and 1,3-cyclohexadiene, react with concentrated acid almost explosively forming tars and sulphur dioxide, whereas dilute acids exert a resinifying action.[110] Butadiene itself, however, is much more resistant to the action of sulphuric acid, being absorbed in 83 per cent acid at about the same rate as propylene.[111] Indeed, the relatively slow rate of absorption of butadienes in sulphuric acid of lower concentrations has been proposed as a basis for the separation of this diolefin from admixed isobutylene and similarly reactive monolefins.[112] In general, the products of the reaction of diolefins with sulphuric acid are tars of ill-defined nature. The observation of Wagner-Jauregg[113] that geranyl acetate results from the action of a mixture of glacial acetic acid and sulphuric acid on isoprene suggests that this is a fruitful field of research.

A more detailed examination of the products of this reaction was made later.[114] A mixture of 450 grams of isoprene, 1500 cc. of glacial acetic acid and 5 grams of concentrated sulphuric acid were allowed to react at room temperature for 3 days. The reaction product, which contained only a small amount of a rubber-like polymer, was hydrolyzed and distilled, yielding 101 grams of a mixture of materials boiling at 72° to 160° C. under 12 mm. pressure. From this mixture, primary alcohols were extracted with phthalic anhydride, tertiary alcohols were removed as borates, leaving a mixture of hydrocarbons. The primary alcohol fraction contained geraniol, cyclogeraniol, and a mixture of sesquiterpené alcohols of the formula $C_{15}H_{26}O$, containing three ethylene linkages in the molecule and boiling mainly at 114° to 126° C. at 0.7 mm. The tertiary alcohol fraction contained *dl*-linalool, *dl*-α-terpineol and sesquiterpene alcohols (also of the composition $C_{15}H_{26}O$) boiling at 108° to 122° C. at 0.43 mm., and the hydrocarbon fraction contained, among other substances, a monocyclic triethylenic hydrocarbon boiling at 120° to 125° C. at 12 mm. This latter compound was converted by boiling 98 per cent formic acid into a dicyclic hydrocarbon of the caryophyllene series.

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[109] *Loc. cit.*

[110] See also Chapter 26 and Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., New York.

[111] Dobrjanski, *Neft. Khoz.*, 1925, 9, 565; *Chem. Abs.*, 1926, 20, 1576.

[112] I. G. Farbenindustrie A.-G., French Patent 703,743, 1930; *Chem. Abs.*, 1931, 25, 4555.

[113] *Ann.*, 1931, 488, 176; *Chem. Abs.*, 1931, 25, 5139.

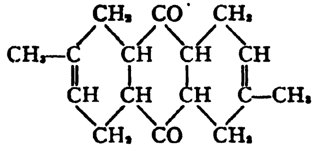
[114] Wagner-Jauregg, *Ann.*, 1932, 496, 52; *Brit. Chem. Abs.* A, 1932, 856.

When shaken with dilute sulphuric acid in the presence of carbon dioxide for 5 days at room temperature, isoprene yields a mixture of hydrocarbons, alcohols, and cyclic ethers (oxides), 1,4-cineol and a small proportion of 1,8-cineol. Evidently, therefore, the action of even dilute sulphuric acid on isoprene is complex, resulting in the formation of a wide variety of products.

Condensation Reactions of Conjugated Diolefins

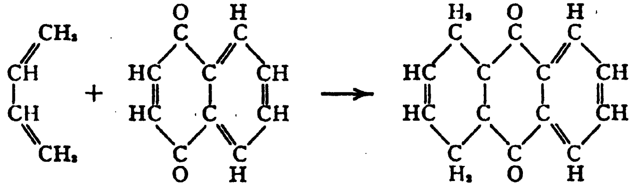
The fact that the simple monolefins react very readily with aromatic hydrocarbons to form alkylated derivatives[115] suggests the possibility that diolefins also would undergo this condensation. Albrecht[116] described several addition products of cyclopentadiene with quinones (cyclopentadiene quinone, the dicyclopentadiene quinone, the cyclopentadiene chloranil and the cyclopentadiene naphthoquinone) without, however, determining their constitution.

Later, von Euler and Josephson[117] found that isoprene could be condensed with benzoquinone by heating in a sealed tube at 120° to 180° C. for 5 to 6 hours to yield a white crystalline substance melting at 234° C., to which they assigned the provisional formula



since it yielded a tetrabromide with bromine in warm acetic acid and a dioxime with alkaline hydroxylamine.

More than twenty years after the original studies of Albrecht, Diels[118] investigated the chemical constitution of these products and discussed the production of these addition products from the diene hydrocarbons. Tetrahydroanthraquinone was obtained from butadiene and α-naphthoquinone,



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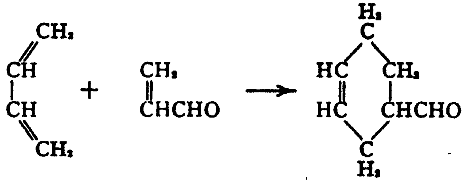
[115] See Chapter 24.

[116] *Ann.*, 1906, 348, 31; *Chem. Soc. Abs.*, 1906, 90 (1), 674.

[117] *Ber.*, 1920, 53B, 822; *Chem. Abs.*, 1920, 14, 3342.

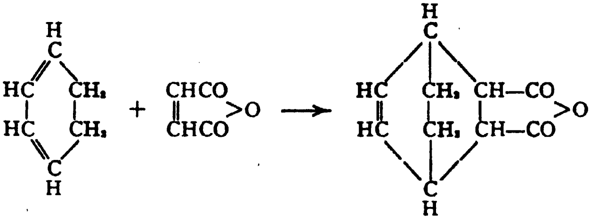
[118] Diels and Alder, *Ann.*, 1928, 460, 98; *Chem. Abs.*, 1928, 22, 1144.

while butadiene and acrolein yielded the tetrahydrobenzaldehyde,

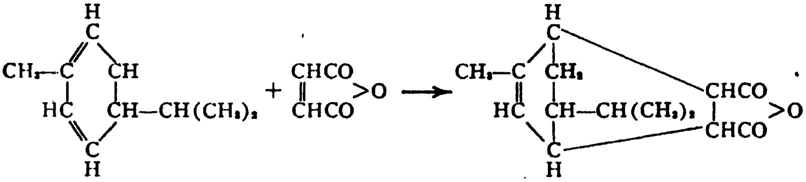


The condensation of butadiene with benzoquinone or its substitution products yielded similar products.[119]

1,2-Dihydrobenzene and maleic anhydride form the endodimethylene tetrahydrophthalic anhydride



and α-phellandrene reacts with maleic anhydride to yield the compound $C_{14}H_{18}O_3$:



It appears from the subsequent work of Alder and his collaborators[120] that these reaction products of maleic anhydride and conjugated dienes can undergo further condensation with the same or other conjugated diolefins to form still more complex molecules containing one double bond. This cumulative condensation (which is analogous to the stepwise polymerization of cyclopentadiene) is exemplified by the combination of butadiene at 140° to 150° C. under pressure (in the presence of benzene as solvent) with 3,6-endomethylene tetrahydrophthalic anhydride. This material is obtained by condensing cyclopentadiene with maleic anhydride, so that the whole synthesis may be expressed graphically as follows:

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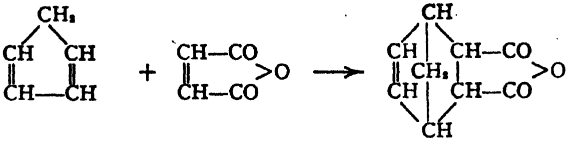
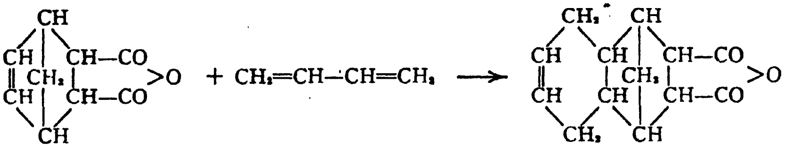
[119] Diels and Alder, German Patent 521.621, 1927; *Chem. Abs.*, 1931, **25**, 3363; British Patent 300,130, 1928; *Brit. Chem. Abs.* **B**, 1930, 549; both patents assigned to I. G. Farbenindustrie A.-G.

[120] Alder and Stein, with Reese and Grassmann, *Ann.*, 1932, **496**, 204; *Brit. Chem. Abs.* **A**, 1932, 938; *Chem. Zentr.*, 1932, **2**, 2048.



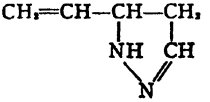
cyclopentadiene *maleic anhydride* *3,6-endomethylene tetrahydrophthalic anhydride*



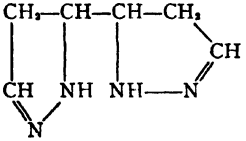
In the same way, 3,6-endomethylene tetrahydrophthalic anhydride can be condensed with isoprene, 1,4-diphenylbutadiene or cyclopentadiene.

The reaction of other diolefins with various unsaturated compounds, such as citraconic and itaconic acid anhydrides, acrylic acid, acrolein and cyclohexanone have also been effected, good yields of condensation products being obtained.[121] Diels and his collaborators[122] also described the production of cyclic nitrogen compounds by the so-called diene-synthesis, for example, that of endomethylene piperidazine from cyclopentadiene and ethyl azodicarboxylate.

According to Müller and Roser,[123] butadiene reacts with diazomethane in absolute ether solution, at —20° C., to yield 5-vinylpyrazoline and then 5,5′-bipyrazoline:



5-vinylpyrazoline



5,5′-bipyrazoline

Similar products are said to be obtained from butadiene and methyldiazomethane and diazoacetic ester.

The importance of the diene-synthesis is indicated by a number of developments. In one process[124] butadiene or other diolefin hydrocarbon is condensed with an aromatic hydrocarbon under slight pressure in the presence of an alkali or alkaline earth metal as a catalyst at somewhat raised temperature. By heating 1 part of butadiene with 3 to 4 parts of toluene at 80° to 90° C. with sodium in an autoclave a colorless liquid hydrocarbon (b.p., 203° to 204° C.) is obtained[125] which is said to have the formula $CH_3CH{=}CHCH_2CH_2C_6H_5$. Isoprene in toluene, when heated in the presence of sodium at 160° C. for 1 hour, yields 5 (or 3)-phenyl-3(or 5)-methyl-2-pentene (b. p., 218° to 222° C.).[126] Under similar conditions, 2,3-dimethylbutadiene yields 5-phenyl-2,3-dimethyl-2-pentene, a liquid boiling at 235° to 238° C., and butadiene and tetrahydronaphthalene condense to a butenyltetrahydronaphthalene boiling at 270° to 272° C,

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[121] For additional information concerning the "diene-synthesis" see Diels, *Z. angew. Chem.*, 1929, 42, 911; *Chem. Abs.*, 1930, 24, 356; *Ann.*, 1929, 470, 62; *Brit. Chem. Abs.* A, 1929, 819; *Ber.*, 1929, 62B, 554; *Brit. Chem. Abs.* A, 1929, 570; *Ber.*, 1929, 62B, 2081; *Brit. Chem. Abs.* A, 1929, 1297. The diene-synthesis has been reviewed also by Downs, *Ind. Eng. Chem.*, 1934, 26, 17.

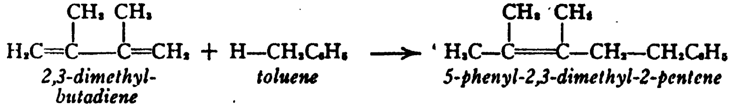
[122] Diels, Blom and Koll, *Ann.*, 1925, 443, 242; *Chem. Abs.*, 1925, 19, 2499. See also Alder and Stein, German Patent 557,338, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 1003.

[123] *J. pr. Chem.*, 1932, 133, 291; *Chem. Abs.*, 1932, 26, 3504.

[124] I. G. Farbenindustrie A.-G., British Patent 315,312, 1929; *Brit. Chem. Abs.* B, 1930, 1103.

[125] Hofmann and Michael, German Patent 557,514, 1928; *Chem. Abs.*, 1933, 27, 514; Swiss Patent 144,850, 1928; *Chem. Zentr.*, 1931, 2, 1055; *cf.* British Patent 315,312, 1929; patents assigned to I. G. Farbenindustrie A.-G.

It appears that direct combination occurs between aromatic hydrocarbons and conjugated diolefins so that 1,4-addition products of the latter are frequently formed. The combination of 2,3-dimethylbutadiene with toluene may thus be represented:



$$H_2C{=}\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H-CH_2C_6H_5 \longrightarrow H_3C-\overset{CH_3}{\overset{|}{C}}{=}\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2C_6H_5$$

2,3-dimethylbutadiene *toluene* *5-phenyl-2,3-dimethyl-2-pentene*

The condensation of quinones with butadiene hydrocarbons appears to be a promising method for the production of anthraquinone and related compounds. Thus, benzoquinone reacts with two molecules of butadiene or its homologues, under the influence of acid or alkaline reagents or by heating, with the production of tetrahydroanthraquinones, which can be oxidized by air in the presence of catalysts if necessary, to yield the corresponding anthraquinones. The condensation product of 1 mole of benzoquinone and 2 moles of isoprene consists of two isomers, one of which is oxidized to 2,6-dimethylanthraquinone by air.[127]

An 80 per cent yield of anthraquinone of excellent purity is said to be formed by the condensation of naphthoquinone with butadiene at 140° C. under pressure in the presence of nitrobenzene. Similarly, 6-methylquinizarin, 6,7-dimethylquinizarin, and 2,3,6,7-tetramethylquinizarin may be prepared.[128]

Diels and Alder [129] produced tetrahydroquinizarins by reaction of naphthazarin or its homologues with conjugated dienes. For example, tetrahydroquinizarin (melting point, 150° to 151° C.) is obtained by heating naphthazarin with butadiene at 50° to 60° C. under pressure in the presence of glacial acetic acid.

A further application of the condensation of the dienes with maleic acid or anhydride is the purification of crude coke-oven benzol.[130] The crude benzol after refluxing with 1 to 3 per cent of the acid or anhydride is distilled. Impurities such as cyclopentadiene, butadiene, and heterocyclic compounds (pyridine) are thus removed. Methylene tetrahydrophthalic anhydride is obtained from the residue and this can be esterified with a polyhydroxy alcohol to yield a resin.[131] The esters of the condensation product from butadiene and maleic anhydride are plasticizers for cellulose esters, according to Brooks and Cardarelli.[131a] Their boiling points are: butyl ester, 186° to 192° C. at 18 mm.; ethyl ester, 133° to 137° C. at 5 mm.; prcpyl ester, 140° to 141° C. at 5 mm.; and secondary-amyl ester, 163° to 165° C. at 5 mm.

The condensation of conjugated diolefins with acid chlorides under the influence of Friedel-Crafts condensing agents takes place vigorously but does not appear to follow the same course as the reaction between monolefins and acid chlorides which results in the ultimate production of vinyl alkyl ketones. According to Wieland and Hasegawa,[182] 1,4-diphenylbutadiene reacts with acetyl chloride in benzene solution and in the presence of aluminum chloride to furnish a white crystalline solid melting at 262° C., corresponding to $C_{30}H_{33}O_2Cl$. Condensation of the same diolefin with benzoyl chloride under similar conditions yields a white crystalline solid which melts at 203° C. and corresponds to $C_{36}H_{30}O$. The constitution of these products is at present unknown but they are probably formed by condensation of benzene as well as of acid chloride with the diolefin accompanied by elimination of hydrogen chloride.

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[126] Hofmann and Michael, *loc. cit.* British Patent 335,512, 1929; *Brit. Chem. Abs.* **B**, 1931, 11; French Patent 667,748, 1929; *Chem. Abs.*, 1930, **24**, 3247; all patents assigned to I. G. Farbenindustrie A.-G.

[127] Lüttringhaus, Neresheimer and Schneider, German Patent 554,878, 1929; *Chem. Abs.*, 1933, **27**, 309; addition to German Patent 494,433, 1928; *Chem. Abs.*, 1930, **24**, 2757; both patents assigned to I. G. Farbenindustrie A.-G.

[128] Kränzlein, Dieterle and Vollmann, German Patent 544,522, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3522.

[129] German Patent 544,523, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3523.

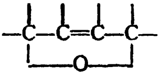
[130] I. G. Farbenindustrie A.-G., British Patent 352,164, 1930; *Brit. Chem. Abs.* B, 1931, 962.

[131] *Cf.* Brooks and Cardarelli, U. S. Patent 1,860,730, May 31, 1932; see Ellis, *Ind. Eng. Chem.*, 1933, **25**, 125.

[131a] U. S. Patents 1,824,068, 1,824,069, 1,824,070, 1,824,071, Sept. 22, 1931; assigned to Petroleum Chemical Corp.; *Brit. Chem. Abs.* **B**, 1933, 219.

MISCELLANEOUS REACTIONS OF CONJUGATED DIOLEFINS

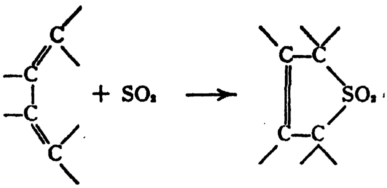
The action of oxygen on conjugated diolefins is very important from the viewpoint of petroleum technology since the gums produced in cracked gasolines on standing are probably oxidized products of such hydrocarbons. The question is dealt with more fully in Chapter 40. The general character of the autoxidation of unsaturated hydrocarbons was clarified by the work of Engler and Weissberg,[183] who demonstrated that the initial products of autoxidation of several monolefins were peroxides containing two atoms of oxygen per molecule. Kogerman[184] recently adduced evidence to show that during the autoxidation of the conjugated diolefins addition of 1 atom of oxygen to each diolefin molecule takes place, the products having some resemblance to the gums of cracked gasolines. Probably addition of oxygen takes place at the 1,4 position with production of substances of the type



The whole subject of autoxidation is very intimately connected with the subject of polymerization since it has been shown that peroxides are highly active catalysts for polymerization of diolefins, styrenes, and analogous bodies.

Diolefins readily form ozonides with ozone. These products play an important rôle in the elucidation of the constitution of diolefins and their derivatives. The conjugated diolefins react very energetically with ozone to furnish monozonides but the diozonides are formed only slowly.

The combination of conjugated diolefin hydrocarbons with anhydrous sulphur dioxide (or in some cases with aqueous solutions of sulphur dioxide or sulphites) is a characteristic reaction which can be used not only for the separation and purification of such hydrocarbons but also for their analytical identification. Monomolecular sulphones, which can be split into their components by heating above about 120° C., are formed according to the general reaction:



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[182] *Ber.*, 1931, 64B, 2516.

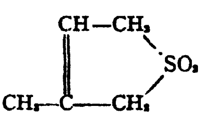
[183] *Ber.*, 1898, 31, 3050.

[184] *Trans. 2nd World Power Conference*, 1930, 8, 33; *Chem. Abs.*, 1931, 25, 5549.

Many of these monomolecular sulphones are well-defined crystalline substances.[134a] It will be noted that this reaction with sulphur dioxide affords yet another example of 1,4 addition to a conjugated system of double bonds. Under certain circumstances polymerized sulphone-like substances are formed instead of the simple monomolecular products.

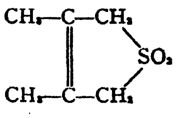
De Bruin,[135] who appears to be one of the first investigators in this field, found that when isoprene was mixed with an equal volume of liquid sulphur dioxide and allowed to stand for 1 to 2 days, a crystalline substance separated which melted without decomposition at 62.5° C. and had the formula $C_5H_8SO_2$. This could be recrystallized from ether and dissolved unchanged in benzene.

On warming a solution of 10 grams of isoprene in 100 cc. of diethyl ether saturated with sulphur dioxide for 5 hours in the water bath, Eigenberger[136] obtained a 60 per cent yield of a monomeric sulphone melting at 63° to 63.5° C. This substance, which was decomposed by heating to 120° to 135° C., readily yielded a dibromide melting at 127° C. when treated with bromine in carbon tetrachloride solution. From a study of various derivatives, Eigenberger assigned to this substance the formula,



Subsequently, he found that this sulphone was converted by the action of aqueous or alcoholic alkali in the presence of radiation from a quartz lamp into an isomeric sulphone, also monomolecular, which melted at 79° C. and was less soluble in ether.[137] The conversion did not take place in the presence of radiation alone and alkali appeared to be essential. On catalytic hydrogenation, the lower melting isomer was found to yield a dihydro-derivative melting at 0.2° C., whereas the higher melting sulphone yielded a dihydro-derivative melting at 0.5° C., showing that the isomerism was the result of a different spatial arrangement of groups around the double bond. To the lower melting isomer Eigenberger[138] assigned a cis-configuration, the other isomer being accordingly assigned a trans-structure. It is interesting to note that the dibromoisoprene sulphone can be readily reduced by zinc and ethyl alcohol to yield 90 per cent of the cis-isomer.

Backer and Bottema[139] obtained a similar monomeric sulphone by treating 2,3-dimethylbutadiene with two molecular proportions of ammonium bisulphite in saturated aqueous solution at 120° C. The product, having the formula



melted at 135° C. and could also be obtained by treating the hydrocarbon with a solution of sulphur dioxide in ether at 100° C. or with sulphurous acid at room temperature. The sulphone could be brominated in benzene solution to yield a dibromide which was readily hydrolyzed by boiling water to a glycol of the formula

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[134a] For information on the x-ray study of the crystalline structure of polymeric and monomeric butadiene sulphones see Sauter, *Z. Krist.*, 1932, 83, 340; *Chem. Abs.*, 1933, 27, 2362.

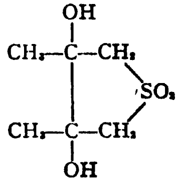
[135] *Proc. K. Akad. Wetensch. Amsterdam,* 1914, 17, 585; *Chem. Soc. Abs.,* 1914, 106 (1), 1197.

[136] *J. prakt. Chem.*, 1930, 127, 307; *Chem. Abs.*, 1931, 25, 276.

[137] Eigenberger, *J. prakt. Chem.*, 1931, 129, 312; *Chem. Abs.*, 1931, 25, 2969.

[138] *J. prakt. Chem.*, 1931, 131, 289; *Chem. Abs.*, 1932, 26, 79.

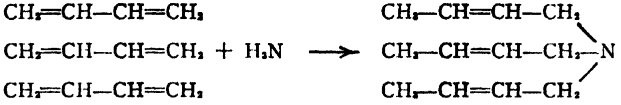
[139] *Rec. trav. chim.*, 1932, 51, 294; *Brit. Chem. Abs.* A, 1932, 361.



melting at 175° C.

Staudinger[140] developed a process for the manufacture of monomolecular sulphones from butadiene hydrocarbons and liquid sulphur dioxide involving the use of 0.5 to 1 per cent of a stabilizing agent or anti-catalyst, which is said to obviate in part the formation of polymerized sulphones. Such stabilizers may consist of polyvalent or other phenols (e.g., hydroquinone, pyrocatechol, and pyrogallol), amines, and metallic copper or its salts. The sulphur dioxide may be employed either in the anhydrous liquid condition or in a solvent such as benzene.

According to Schmidt, Fries and Kollek,[141] conjugated diolefins react with ammonia and amines in the presence of an alkali metal or of alumina, magnesia, or barium chloride, to form unsaturated organic bases which can be used in the vulcanization of rubber and as insecticides. For example, a solution of sodium in liquid ammonia is allowed to react with butadiene at —80° C. for 10 days and then at —15° C. for 5 days more, when the products are found to consist of tributenylamine and higher bases. By conducting a gaseous mixture of vinyl acetate and monomethylamine over bauxite at 300° C. a mixture of unsaturated bases is produced. Assuming 1,4 addition to take place, the condensation of ammonia and butadiene may perhaps be represented as follows:



tributenylamine

Conjugated diolefins may be directly ethylated by reaction of an ethereal solution of 2 moles of ethyl bromide, or 1 mole of ethyl sulphate, with a mixture of 2 moles of potassium and 1 mole of the diolefin. Midgley and Henne[142] observed that ethylation of isoprene by this method gave a comparatively poor yield of 4-methyl-4-octene, $CH_3CH_2CH_2—C(CH_3)=CHCH_2CH_2CH_3$.

Lebedev and Yakubchik[143] made a study of the hydrogenation of twelve typical butadiene hydrocarbons in the presence of platinum black (Willstätter) in alcohol and concluded that three different reactions may be postulated, namely:

(1) Hydrogenation in two consecutive stages, in the first of which 1,4 addition of hydrogen atoms takes place and in the second, addition to the resulting 2,3-bond, which occurs at a different reaction velocity. Conjugated diolefins of the general formula

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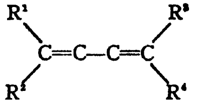
[140] German Patent 506,839, 1929; *Chem. Abs.*, 1931, **25**, 522; French Patent 698,857, 1930; *Chem. Abs.*, 1931, **25**, 3360; British Patent 361,341, 1930; *Brit. Chem. Abs.* **B**, 1932, 301.

[141] German Patent 528,466, 1928; *Chem. Abs.*, 1931, **25**, 4555; French Patent 662,431, 1928; *Chem. Abs.*, 1930, **24**, 377; both patents assigned to I. G. Farbenindustrie A.-G.

[142] *J.A.C.S.*, 1930, **52**, 2075.

[143] *J.C.S.*, 1928, 823, 2190.



in which R^1, R^2, R^3, and R^4 are alkyl groups (e.g., diisobutenyl), are hydrogenated in this manner.

(2) The first two hydrogen atoms add to the diene molecule in all three possible positions (i.e., 1,2; 3,4; and 1,4) and further hydrogenation takes place simultaneously with the formation of fully saturated molecules. This reaction, which is exhibited by butadiene, isoprene, piperylene and diisopropenyl, is of a complicated nature.

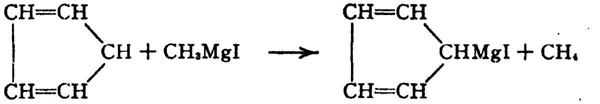
(3) The possible immediate addition of two hydrogen molecules at such a high velocity that the intermediate monolefin has but a transitory existence. Though this is theoretically possible, no examples of this reaction were observed.

The condensation of isoprene with amylene, pinene, trimethylethylene, isopinene, dipentene and sylvestrene in the presence of aluminum chloride has been noted by Aschan.[144] Recently, Thomas and Carmody[145] found that, though pure isoprene does not immediately condense under the influence of aluminum chloride, the presence of a small amount of a monolefin such as 2-pentene immediately initiates a violent reaction. From the reaction of isoprene with monolefins in the presence of aluminum chloride, Thomas and Carmody have been able to obtain synthetic resins of promise. The procedure has already been discussed more fully in Chapter 6.[146]

CONDENSATION REACTIONS OF CYCLOPENTADIENE

Cyclopentadiene, one of the most highly reactive of the conjugated diolefins, deserves special mention because of its great power of condensation with a large number of organic substances, some of which have already been mentioned. Its condensation with itself to yield the dimer, dicyclopentadiene, occurs spontaneously at ordinary temperature[147] and is apparently catalyzed by autoxidation products, though not by light.[148] Condensation to a tetramer and heavier polymers also occurs.[149]

Cyclopentadiene is resinified by dilute acids and alkalies and strong sulphuric acid reacts with it explosively. The great reactivity of the CH_2 group of the hydrocarbon has been ascribed by Thiele[150] to the presence of the contiguous unsaturated linkages. One hydrogen atom of the CH_2 group is replaceable by potassium. The hydrocarbon reacts with methyl magnesium iodide according to the equation:



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[144] *Öfversigi Finska Vetenskaps Soc.*, 1916, **58**, 42; *Chem. Abs.*, 1920, **14**, 3823.

[145] *J.A.C.S.*, 1932, **54**, 2480; *Ind. Eng. Chem.*, 1932, **24**, 1125.

[146] See also Chapter 26.

[147] Kraemer and Spilker, *Ber.*, 1896, **29**, 552; Wieland, *Ber.*, 1906, **37**, 1492; Stobbe and Reuss, *Ann.*, 1912, **391**, 151; *Chem. Abs.*, 1912, **6**, 3275.

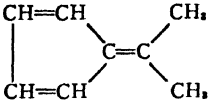
[148] Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436.

[149] Staudinger and Rheiner, *Helv. Chim. Acta*, 1924, **7**, 23; Staudinger and Bruson, *Ann.*, 1926, **447**, 97, 110; *Chem. Abs.*, 1926, **20**, 2148; Bruson and Staudinger, *Ind. Eng. Chem.*, 1926, **18**, 381; Lebedev and Merezkovski, *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1249; *Chem. Abs.*, 1914, **8**, 320; see Chapter 26 also.

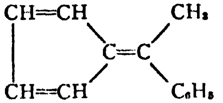
[150] *Ber.*, 1900, **33**, 666; *ibid.*, 1901, **34**, 68.

The CH_2 group of the cyclopentadiene ring condenses, under the influence of sodium ethylate, with a large variety of ketones and aldehydes to form the highly colored hydrocarbons of the fulvene series:[151]

With acetone



With acetophenone



Cyclopentadiene condenses with unsaturated nitriles at 150° to 160° C. under pressure to yield cyclic nitriles. The product of the condensation of cyclopentadiene and crotononitrile is said to be a dicyclic nitrile boiling at 87° to 88.5° C. at 12 mm.[152]

Analytical Reactions of Conjugated Dienes

The analytical methods for the determination of unsaturated hydrocarbons by bromine or iodine addition values are unsuitable for the estimation of diolefins since these hydrocarbons behave under the conditions of those determinations as monolefins and add only two, instead of four, halogen atoms. Thus the McIlhiney bromine value of a pure sample of isoprene was found to be 234.7 instead of the theoretical 469.5 for two double bonds.[153] On the other hand, Dobrjanski[154] made use of the bromide-bromate reagent of Francis for estimating butadiene in gas mixtures containing monolefins and stated that tetrabromides were formed from the diolefins and dibromides from the monolefins. It has been shown,[155] however, that the diolefins readily add four atoms of hydrogen on catalytic hydrogenation at low temperatures and that this hydrogen addition value may be utilized to ascertain the purity of isoprene and other diolefins such as isoprene.

For the analytical determination and identification of the diolefins in hydrocarbon mixtures, the halogen derivatives have been most frequently employed, more especially the tetrabromides. The tetrabromide of butadiene was used to identify that hydrocarbon in a complex mixture of hydrocarbons of "oil gas" by Armstrong and Miller[156] and subsequently by Schütz[157] in the case of low-temperature carbonization gas. A determination of butadiene in the gas from low-temperature carbonization processes by conversion into the tetrabromide has been described by Manning, King and Sinnatt.[158] The method consisted in passing a known volume of the hydrocarbon mixture through bromine and water. When the scrubbing was complete the mixed bromides were freed from excess bromine by washing with dilute caustic soda, and were then distilled into 3 fractions as follows:

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[151] Thiele, *Ber.*, 1900, 33, 666; *ibid.*, 1901, 34, 68; Thiele, Balhorn and Albrecht, *Ann.*, 1906, 348, 1; *Chem. Soc. Abs.*, 1906, 90 (1), 639.

[152] I. G. Farbenindustrie A.-G., British Patent 341,047, 1929; *Brit. Chem. Abs.* B, 1931, 385; addition to British Patent 300,130, 1928; *Brit. Chem. Abs.* B, 1930, 549.

[153] Waterman and van Westen, *Rec. trav. chim.*, 1929, 48, 1084; *Brit. Chem. Abs.* A, 1930, 58.

[154] *Neft. Khoz.*, 1925, 9, 574; *Chem. Abs.*, 1926, 20, 1577.

[155] Waterman and van Westen, *loc. cit.*

[156] *J.C.S.*, 1886, 49, 74.

[157] Schütz, Buschmann and Wissebach, *Ber.*, 1923, 56, 869.

[158] *Dept. of Sci. and Ind. Research* (Brit.), *Tech. Paper* 19, 1928; *Chem. Abs.*, 1928, 22, 1668.

(1) Below 80° C. at 20 mm. (ethylene, propylene and butylene dibromides);
(2) 80° to 130° C. at 20 mm. (some butylene dibromide and bromine derivatives of higher olefins);
(3) Residue.

The residue from the distillation (containing acetylene tetrabromide and butadiene tetrabromides) was extracted with hot alcohol. The filtered solution was cooled to 0° C., and the solid crystalline butadiene tetrabromide (m.p., 118° C.) which separated was rapidly filtered, dried, and weighed. Experiments with pure butadiene showed that the two forms of the tetrabromide were produced in about equal amounts, so that to obtain the total tetrabromide present the weight of the higher melting form, obtained as described above, must be doubled. The higher melting tetrabromide, though soluble in hot alcohol, separates almost completely from that solvent at 0° C.

According to Sorokin and Belikov,[159] a more accurate method of determining butadiene in gas mixtures is to separate it in the form of its tetrachloride by passing the gas through a saturated solution of chlorine in carbon tetrachloride. The butadiene tetrachloride (b.p., 118° to 122° C.) is separated from other dichlorides by fractionation and weighed.

The analytical estimation or identification of diolefins in the form of their tetrabromides has the obvious advantage that it permits the regeneration of the diolefins by reduction with zinc and alcohol. A limitation of this method, however, is that many of the diolefins, particularly isoprene, cyclopentadiene, and the dimethylbutadienes, form liquid tetrabromides. Nevertheless, both piperylene and butadiene furnish easily crystallizable tetrabromides, useful for identification purposes.

As previously mentioned, to estimate isoprene in a mixture of butenes, pentenes and benzene, Ostromislensky[160] converted the former hydrocarbon into its dihydrochloride by shaking it with concentrated hydrochloric acid for 6 hours. The products of reaction were carefully washed, dried, and then fractionated, the fraction boiling at 130° to 140° C. being fairly pure isoprene dihydrochloride (2,4-dichloro-2-methylbutane). The applicability of this method is probably limited to mixtures containing comparatively high concentrations of isoprene.

Perhaps the most promising method for the positive identification and possibly the estimation of conjugated diolefins is that based upon the previously discussed combination of these hydrocarbons with maleic anhydride.[161] The importance of this reaction, from the analytical standpoint, is that the reaction products are easily crystallized and have characteristic melting points, so that they are of unusual value for purposes of identification. The products of the reaction between conjugated diolefins and maleic anhydride are acid anhydrides, some of which can be hydrolyzed to the corresponding acid by boiling water. The ease of formation of these condensation products with maleic anhydride varies considerably. The cyclic diolefins, 1,3-cyclopentadiene and 1,3-cyclohexadiene, react energetically with maleic anhydride at 0° C. to give almost quantitative yields. Butadiene, isoprene and piperylene react slowly with maleic anhydride in the cold and some polymerization of the two latter hydrocarbons occurs. With butadiene, heating under pressure to about 100° C. is apparently necessary to complete reaction. According to Farmer and Warren,[162] a 95 per cent yield of the addition product of piperylene and maleic anhydride is obtained by allowing the mixed reactants, dissolved in benzene, to stand at 0° C. for 5 days. If higher temperatures are employed, pronounced polymerization occurs. Under similar conditions, 1,2-dimethylbutadiene furnishes a 96 per cent yield of the condensation product but 1,1-dimethylbutadiene yields only polymerized products even at low temperatures. The melting points of some of these reaction products of maleic anhydride are given in Table 116.[163]

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[159] *J. Chem. Ind. Russia,* 1925, 1, 28; *Chem. Abs.,* 1926, **20**, 352.

[160] *J. Russ. Phys.-Chem. Soc.,* 1915, 47, 1978; *Chem. Abs.,* 1916, **10**, 1341.

[161] Diels and Alder, *Ann.,* 1928, 460, 98; *Chem. Abs.,* 1928, **22**, 1144; Diels, Alder, with Lübbert, Naujoka, Querberitz, Röhl and Segeberg, *Ann.,* 1929, 470, 62; *Chem. Abs.,* 1929, **23**, 3692.

[162] *J.C.S.,* 1931, 3221.

TABLE 116.—*Melting Points of Addition Products with Maleic Anhydride or Acid.*

Hydrocarbon	Anhydride ° C.	Acid ° C.
1,3-Butadiene	103–104	166
1-Methylbutadiene (piperylene)	62	155
2-Methylbutadiene (isoprene)	63–64	—
1,2-Dimethylbutadiene	67	—
1,3-Dimethylbutadiene	56–57	—
1,4-Dimethylbutadiene	95–96	—
2,3-Dimethylbutadiene	78–79	—
Trimethylbutadiene	49	—
1,3-Cyclopentadiene	164–165	177–179
1,3-Cyclohexadiene	147	—

The maleic anhydride condensation provides a satisfactory method for the identification of a number of conjugated diolefins in mixtures. The method has been used by Birch and Scott[164] for the identification of conjugated diolefins (butadiene, isoprene, piperylene and cyclopentadiene) in the lower fractions of vapor-phase cracked gasoline. Unfortunately, its applicability as a quantitative method of estimation appears to be limited, except perhaps in the case of conjugated cyclic diolefins which react readily and quantitatively with this reagent. However, Bassett and Williams[165] applied the condensation with maleic anhydride to the quantitative estimation of isoprene in the products of distillation of rubber, using a procedure essentially similar to that of Farmer and Warren. The method was more satisfactory than other proposed modes of estimation, which were found to yield low results.

It has previously been shown[166] that under controlled conditions, conjugated diolefins can combine with sulphur dioxide to yield well-defined crystalline monomolecular sulphones. It would appear that such sulphones might be of value in the identification of conjugated diolefins in hydrocarbon mixtures. The sulphones can be reconverted into their parent substances by heating to temperatures above about 120° C. Lebedev and Yakubchik[167] proposed a method of estimating isoprene, based upon the formation of a sulphone on treatment with sulphur dioxide, but Bassett and Williams[168] find that this method yields results which are too low.

OTHER DIOLEFINS

The 1,4- and 1,5-diolefins do not appear to be formed to any appreciable degree during the pyrolysis of petroleum hydrocarbons. They are of importance, however, in the chemistry of the essential oils and perfumes. A number of the 1,4-diolefins have been studied by Shoemaker and Boord.[169] The 1,5-diolefins are of interest because of their conversion by the action of 70 per cent sulphuric acid into an oxide, the anhydride of the 2,5-glycol, which contains a 5-membered heterocyclic ring.[170]

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[163] Diels and Alder, *loc. cit.* See also Alder, "Die Methoden der Dien-Synthese," Berlin, 1933.
[164] *Ind. Eng. Chem.*, 1932, **24**, 49.
[165] *J.C.S.*, 1932, 2324.
[166] Staudinger, *loc. cit.*
[167] *J.C.S.*, 1928, 823.
[168] *J.C.S.*, 1932, 2324.
[169] *J.A.C.S.*, 1931, **53**, 1505.

When 1,5-hexadiene (diallyl) is treated with 100 per cent sulphuric acid at —15° C. to +4° C. the production of diallyl ether is not noticeable, the two main products being a crystalline neutral cyclic monoester and a diester. These substances are easily hydrolyzed to the 2,5-glycol, which is unstable in the presence of acids and tends to dehydrate, thus forming diallyl oxide.[171]

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[170] Pogorzhelsky, *J. Russ. Phys.-Chem. Soc.*, 1898, **30**, 977; *Chem. Soc. Abs.*, 1899, **76** (1), 785.
[171] Cortese, *Ber.*, 1929, **62B**, 504; *J.A.C.S.*, 1929, **51**, 2266.

Chapter 28

Important Reactions of Acetylene. Production of Acetaldehyde and Vinyl Esters

The hydrocarbon acetylene is the simplest member of a series of hydrocarbons, called the acetylenes or alkynes, possessing the general formula C_nH_{2n-2} and characterized by a triple-bonded carbon linkage. Acetylene itself is $HC{\equiv}CH$, while two series of homologues exist, in which either one, or both, of the hydrogen atoms of the acetylene molecule are replaced by alkyl groups.

Because of the extraordinary breadth of reactivity of acetylene,[1] it stands forth as one of the most promising hydrocarbons to be considered as a source of chemical products. Since it can be obtained from natural gas or cracked petroleum gases by pyrolysis (discussed in Chapters 4 and 9) or oxidation (Chapter 39), as well as from calcium carbide manufactured from coal and lime, its importance in this regard is assured and bids fair to create for this hydrocarbon a status in the aliphatic as important as that occupied by benzene in the aromatic series.

MANUFACTURE OF ACETYLENE

The acetylene of commerce has been obtained chiefly by the hydrolysis of calcium carbide, a compound produced in immense quantities by heating lime and carbon (e.g., coke) together to a very high temperature in the electric furnace. On treatment with water, calcium carbide is decomposed according to the equation:

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

a reaction discovered by Wöhler in 1862.[1a] Some 30 years after this discovery, the commercial production of calcium carbide in the electric furnace was begun and since that time the carbide industry has grown in magnitude and importance. As the manufacture of calcium carbide on a large scale demands a cheap and plentiful supply of electrical energy, carbide factories are entirely located in districts where water power can be utilized for the generation of the necessary electrical power.

Acetylene is produced to a greater or less extent by the decomposition of a large number of metallic carbides by water or by dilute mineral acids. The carbides of calcium, barium, strontium, or of lithium, sodium, potassium, caesium and rubidium, having the formulas $M^{II}C_2$ or $M^I_2C_2$, are all decomposable by water to yield acetylene in a more or less pure condition. Certain other carbides, such as carbides of manganese, iron, cerium, and thorium, furnish mixtures of saturated and unsaturated hydrocarbons (including acetylene), while aluminum and beryllium carbides furnish almost pure methane on decomposition by water.[2] The production of acetylene-forming carbides by heating metallic oxides in methane at high temperatures has been described by Fischer and Bangert.[3]

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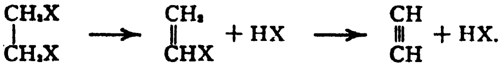
[1] The properties of acetylene are reviewed by Miloslavskii and Glizmanenko (*Avtogennoe Delo*, 1932, No. 4, 17; No. 6. 3; *Chem. Abs.*, 1932, 26, 5544).

[1a] *Ann.*, 1862, 124, 220.

Of considerable scientific interest is the direct synthesis of acetylene by the passage of hydrogen between the poles of a carbon electric arc.[4] The electrical decomposition (by means of either low- or high-tension arcs) of many hydrocarbons, a subject discussed in Chapter 9, similarly yields considerable quantities of acetylene together with other hydrocarbons. During recent years much interest has been aroused in the commercial production of acetylene by the high-temperature pyrolysis of methane and other saturated hydrocarbons. It appears that very high temperatures (above 1000° C. and up to 3000° C.) in conjunction with very short periods of heating are the conditions most favorable to good yields of acetylene. Acetylene may also be produced by the incomplete combustion of hydrocarbons such as methane or natural gas, with air or oxygen at high temperatures. The formation of acetylene by all these high-temperature methods is connected with the fact that acetylene has increased stability with rising temperature as shown by thermodynamic calculations. Though it is very doubtful if acetylene ever becomes perfectly stable with respect to its elements even at the highest temperatures, it appears that an equilibrium of the type $2C\ (gas) + H_2 \rightleftarrows C_2H_2$ is set up, in which the point of equilibrium tends more towards the acetylene side of the equation as the temperature is increased.

Very pure acetylene may be produced by the decomposition of copper acetylide (made by passing crude acetylene into an ammoniacal cuprous salt solution) with potassium cyanide.[5] If mineral acids are used to decompose this acetylide, relatively small yields of acetylene are formed and considerable amounts of by-products result. Acetylene may be obtained from a large number of halogenated hydrocarbons. Thus, acetylene tetrachloride or tetrabromide are readily reduced to acetylene by treatment with metallic zinc,[6] while iodoform and bromoform also yield this hydrocarbon by the action of metallic copper or zinc or of the zinc-copper couple[7] of Gladstone and Tribe. The ethylene dihalides can be converted into acetylene either by the action of hot alcoholic potash[8] or by pyrolysis at moderately high temperatures. In each case a vinyl halide is formed as an intermediate compound and the reactions may be represented as follows:



$$\begin{matrix} CH_2X \\ | \\ CH_2X \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CHX \end{matrix} + HX \longrightarrow \begin{matrix} CH \\ \| | \\ CH \end{matrix} + HX.$$

A number of other methods of preparation are known, including the electrolysis of unsaturated carboxylic acids, but these are of little practical interest.

The carbide process is possibly the most widely used, although the electrical decomposition and the thermal decomposition of gaseous hydrocarbons to produce acetylene are being developed on a commercial scale. The electrical decomposition of higher boiling petroleum fractions, such as fuel oil, also leads to the formation of acetylene together with ethylene and other unsaturated hydrocarbons. In localities where cheap supplies of electrical energy and natural gas are available, the production of acetylene and hydrogen together with carbon black, ethylene and other by-products should be economical.

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[2] For a review of the formation of hydrocarbons from carbides see Tropsch, *Ges. Abhandl. Kennt. Kohle*, 1917, 2, 203.

[3] *Brennstoff-Chem.*, 1929, 10, 261; *Chem. Abs.*, 1930, 24, 3453. *Cf.* also Peters and Meyer, *Brennstoff-Chem.*, 1929, 10, 324; *Chem. Abs.*, 1930, 24, 484.

[4] Berthelot, *Compt. rend.*, 1862, 54, 640; *Ann.*, 1862, 123, 212; *Ann. chim. phys.*, 1901, (7) 23, 444; *ibid.*, 1905, (8) 6, 182; *Chem. Soc. Abs.*, 1901, 80 (2), 685; Bone and Jerdan, *J.C.S.*, 1897, 71, 41; *ibid.*, 1901, 79, 1042; Pring and Hutton, *J.C.S.*, 1906, 89, 1600; von Wartenburg, *Z. anorg. Chem.*, 1907, 52, 310; *Chem. Abs.*, 1907, 1, 1122.

[5] Baeyer, *Ber.*, 1885, 18, 2273; Zeisel, *Ann.*, 1878, 191, 368; *Chem. Soc. Abs.*, 1878, 34, 653; Römer, *Ann.*, 1886, 233, 182; *Chem. Soc. Abs.*, 1886, 50, 845; Noyes and Tucker, *Amer. Chem. J.*, 1897, 19, 123; *Chem. Soc. Abs.*, 1897, 72, 261.

[6] Sabanejev, *Ann.*, 1883, 216, 241, 251; *Chem. Zentr.*, 1883, 482.

[7] Cazeneuve, *Compt. rend.*, 1883, 97, 1371; *Chem. Soc. Abs.*, 1884, 46, 418. *Compt. rend.*, 1891, 113, 1054; *Chem. Soc. Abs.*, 1892, 62, 421.

[8] Savitsch, *Jahresber.*, 1861, 646.

PURIFICATION AND SEPARATION OF ACETYLENE

The purity of acetylene obtained by interaction of calcium carbide and water depends mainly on the purity of the carbide used. The impurities actually present in acetylene, so generated, consist mainly of phosphine, hydrogen sulphide, ammonia, and very small amounts of silicon hydrides. The actual proportion of these impurities is usually relatively very small but their objectionable nature renders their removal imperative for a number of purposes. Scrubbing with water is usually sufficient to reduce the quantities of all impurities, except phosphine, below the limit necessary for safe application. Phosphine is removed by oxidation (to phosphoric acid) with reagents such as bleaching powder, or acid solutions of chromic acid. Acid solutions of cuprous salts, with which phosphine and sulphuretted hydrogen readily combine to yield copper phosphide or sulphide, have also been employed.

For the separation of acetylene from the gaseous mixture obtained by high-temperature pyrolysis or electrical disintegration of hydrocarbons, a number of methods have been proposed, some of which have already been discussed in Chapters 4 and 9. Hull[9] recovered acetylene from gas mixtures by scrubbing them in stages with a sulphuric acid solution of mercuric sulphate under successively higher pressures. Solvents[10] for recovering acetylene are esters or ethers boiling above 100° C., particularly an ester, ether, or ester-ether of a polyhydric alcohol, such as glycol monoformate, glycol mono- and dialkyl ethers, esters of monoalkyl ethers of ethylene glycol, glycerol mono- and diacetates, glycerol ethers, esters of glycerol mono- or dialkyl ethers, phthalate esters of glycol ethers, and ethyl lactate. Liquefied sulphur dioxide, ammonia, carbon dioxide, and methyl and ethyl chlorides have also been suggested for the extraction of acetylene.[10a]

A method for purification of acetylene in the presence of other unsaturated hydrocarbons such as diacetylene, ethylene, allene, butylene, isoprene, butadiene and cyanogen compounds has been developed.[11] The cyanogen compounds are removed by washing with solutions of ferrous sulphate, sodium or potassium hydroxide and the gases are then passed over activated carbon or silica gel to remove other impurities. The gas is then ready for conversion into acetaldehyde by absorption in sulphuric acid in the presence of mercury or in other ways. In another process the acetylene is frozen out between a temperature of —30° and —81° C.[11a]

PHYSICAL PROPERTIES OF ACETYLENE

Pure acetylene is a colorless gas having a pleasant ethereal odor. At low temperatures it solidifies to a white crystalline mass, m.p. —81.5° C. and sublimation point —83.6° C.[12] Liquid acetylene boils at —88.5° C. according to McIntosh and Maass,[12] but other workers give the following temperatures: —82.4° C.[13] and —84.0° C.[14] Its critical constants are as follows: critical temperature 37.05° C.; critical pressure 68.0 atmospheres, and critical volume 83 cc.

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[9] British Patent 331,610, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 978.

[10] Horsley and Roffey, British Patent 331,654, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 978.

[10a] I. G. Farbenindustrie A.-G., French Patent 724,476, 1931; *Chem. Abs.*, 1932, **26**, 4823.

[11] I. G. Farbenindustrie A.-G., British Patent 340,787, 1929; *Chem. Abs.*, 1931, **25**, 4012. French Patent 688,186, 1930; *Chem. Abs.*, 1931, **25**, 752.

[11a] I. G. Farbenindustrie A.-G., British Patent 371,142, 1931; *Brit. Chem. Abs.* **B**, 1932, 762; French Patent 724,293, 1931; *Chem. Abs.*, 1932, **26**, 4829.

Acetylene is a very highly endothermic compound, its heat of formation from its elements at constant pressure and volume being about —50 kg. cals. For this reason it has a great tendency to decompose, and compression of gaseous acetylene beyond a certain pressure results in violent explosions. According to the determinations of Rimarski,[15] pure acetylene undergoes explosive decomposition at pressures in excess of atmospheric varying from 1.1-1.3 atmospheres, 0.80-0.85 atmosphere, and 0.50-0.55 atmosphere in tubular containers of 3.8 cm., 6.6 cm., and 25 cm. bore, respectively. When acetylene is diluted with other gases such as hydrogen or hydrocarbons the tendency to explode is very greatly diminished and such gas mixtures may be compressed to fairly high pressures without danger of explosion. Thus a mixture of oil-gas and 20 to 40 per cent acetylene is reported not to be explosive under 7 atmospheres pressure.

Since acetylene cannot, like other gases, be stored in cylinders under high pressure, some safe method of storage in concentrated form had to be adopted. Claude and Hess[16] in 1896 proposed to overcome the difficulty by making use of the very high solubility of acetylene in acetone, which dissolves 24 volumes of acetylene at 15° C. and 1 atmosphere, but it was found that the danger of explosion, though greatly minimized by such solution, was not entirely obviated. The problem was finally solved by Janet and Fouche,[17] who showed that when acetylene is dissolved in acetone previously adsorbed by a porous material of the right kind under 10 atmospheres pressure, then pressures up to 150 lbs. per sq. in. may be applied with safety.

The solubility of acetylene in many liquids is very considerable, especially in organic liquids of the ketone class. It is soluble in water to the extent of about 1 volume per volume of water at 12° C.[18] Alcohol and acetic acid dissolve 6 volumes of the gas and chloroform and benzene 4 volumes, per volume of solvent. Its very great solubility in acetone has previously been noted. Acetaldehyde has also been suggested since it dissolves half its own weight of gas.[18] According to Roffey[19] acetylene may be stored in cylinders containing solid absorbent material impregnated with solvents consisting of a relatively non-volatile ether, ester, or ether-ester of a polyhydric alcohol, or mixtures of these. Before storing, the acetylene is preferably dried by passing over calcium chloride before and after compression.

Pure acetylene has little action on metals but crude acetylene readily attacks copper with the formation of the explosive acetylide. Since nickel and tin are both resistant to the action of this gas, coatings of these metals are recommended where exposure to acetylene is contemplated.

[12] McIntosh, *J. Phys. Chem.*, 1907, 11, 306; *Chem. Abs.*, 1907, 1, 1844; Maass and McIntosh, *J.A.C.S.*, 1914, 36, 737; International Critical Tables gives the m.p. as —81.8° C.

[13] Ladenburg and Krügel, *Ber.*, 1899, 32, 1821; 1900. 33. 638.

[14] Burrell and Robertson, *Bur. Mines Tech. Paper*, 142, 1916. *Chem. Abs.*, 1917, 11, 311.

[15] *Autogene Metallbearbeitung*, 1926, 19, 269.

[16] *Compt. rend.*, 1897, 124. 626; *J.S.C.I.*, 1897, 16, 524.

[17] See Thorpe, "Dictionary of Applied Chemistry," Longmans, Green & Co., Ltd., London, 1912, 1, 33. Advantage has been taken of the explosibility of various acetylene derivatives, in particular, diacetylene, to reduce the temperature of spontaneous ignition of Diesel fuels (I. G. Farbenindustrie A.-G., British Patent 399,150, 1932).

[18] James and Watson, U. S. Patent 928,867, July 20, 1909; James, *Ind. Eng. Chem.*, 1913, 5, 115.

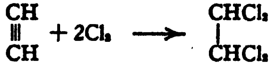
[19] British Patent 335,820, 1929; to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, 25, 1662.

CHEMICAL PROPERTIES OF ACETYLENE

Acetylene is a hydrocarbon possessing very great chemical reactivity and power of condensation. From a thermodynamic standpoint this high reactivity is the result of its relatively great internal energy content. The acetylene molecule may, perhaps, be compared to a high explosive which only needs some slight impetus (in the form of a catalyst or an energy excitation) to enable it to release its store of chemical energy.

As a typical unsaturated hydrocarbon, acetylene readily undergoes a vast number of *addition* reactions not only with halogens, halogen acids and organic acids, but also, under proper conditions, with water, alcohols, ammonia and numerous organic compounds. It also combines with a great number of inorganic substances, notably with hydrogen sulphide, hydrogen cyanide, sulphuric acid, and many metallic salts.

Its addition reaction with chlorine, considered in detail later, is typical of the acetylene hydrocarbons as a class. Four atoms of chlorine are ultimately added to yield acetylene tetrachloride, thus:



$$CH{\equiv}CH + 2Cl_2 \longrightarrow CHCl_2{-}CHCl_2$$

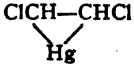
On hydrogenation, acetylene yields first ethylene and finally ethane. The condensations of acetylene with water, chlorine, halogen acids and organic acids are of industrial importance.

Some of the characteristic reactions of acetylene are those with the salts of silver, copper and mercury. When acetylene is passed into an ammoniacal solution of a silver or cuprous salt, the so-called acetylides of these metals are formed. Silver acetylide is a yellowish precipitate of the composition $C_2Ag_2.H_2O$, while cuprous acetylide is a brick-red precipitate of the formula $Cu_2C_2.H_2O$, which may be dehydrated to Cu_2C_2 by gently warming. All the acetylides are highly unstable and explode with violence on heating, or, when dry, under the influence of slight mechanical agitation. The formation of explosive metallic derivatives is characteristic of hydrocarbons containing a hydrogen atom linked to a triple-bonded carbon atom, i.e., containing the group $—C{\equiv}CH$. These include not only acetylene and the monoalkylacetylenes but also diacetylene $HC{\equiv}C—C{\equiv}H$, and its monoalkyl derivatives.

The products obtained by treating mercury salts with acetylene are of importance because these compounds are employed industrially in the preparation of acetaldehyde from acetylene. They may be briefly summarized by the following cases.

Passage of acetylene through aqueous solutions of *mercuric* salts leads to the production of white precipitates which on warming with water, or on treatment with acids, furnish good yields of acetaldehyde. Thus mercuric acetate solutions give a slimy non-explosive white precipitate of the composition $3C_2Hg.2Hg(OH)_2$; while a saturated solution of mercuric chloride in alcohol furnishes a white, crystalline addition product, m.p. 113° C., of the formula $HgCl_2.C_2H_2$ and possible constitutions [20]

$ClHgCH{=}CHCl$ or



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[20] Chapman and Jenkins, *J.C.S.*, 1919, 115, 847.

Aqueous solutions of mercuric chloride yield an amorphous, white precipitate of the formula $C_2Hg.HgCl_2$ (also possibly $(HgCl)_3.C.CHO$) which, on heating in aqueous suspension, furnishes a practically quantitative yield of acetaldehyde.[21] It appears certain that these addition products with mercuric salts, in non-alkaline solutions, are the intermediates in the synthesis of acetaldehyde by the liquid-phase process. On passing acetylene into alkaline solutions of mercuric salts (e.g., Nessler solution), a white, very explosive *mercuric acetylide* of the formula C_2Hg is formed.[22] Treatment of this substance with acids regenerates acetylene.

Mercurous acetylide, a gray explosive precipitate of the formula $C_2Hg_2.H_2O$, is made by passing acetylene through an aqueous solution of mercurous acetate in the dark.[23]

From solutions of gold, palladium and osmium, acetylene precipitates the metals either in the free state or as double compounds but the gas does not appear to react with the salts of iron, nickel, cobalt, lead, cadmium, platinum, iridium, rhodium, zinc, arsenic, or tin.

INDUSTRIAL UTILIZATION OF ACETYLENE

In the early stages of the carbide industry the chief interest lay in the utilization of the acetylene, produced therefrom, for illuminating purposes. Although even today considerable quantities of carbide are employed for acetylene lighting, the main applications of acetylene gas are, first, in autogenous welding (by means of the oxy-acetylene flame) and, second, as a raw material for the manufacture of a wide variety of organic chemicals, which include numerous halogen compounds as well as acetaldehyde, acetic acid, acetone and vinyl derivatives. The progress in the field of the chemical utilization of acetylene since 1910 has been exceptionally rapid.

Later, attention was directed to the possible utilization of acetylene as a raw material for the manufacture of synthetic rubber-like substances. In the following pages an account is given of some of the more important reactions of acetylene.

POLYMERIZATION OF ACETYLENE

Berthelot and Gaudechon[24] observed that ultraviolet rays from a mercury arc caused partial polymerization of acetylene to a yellow solid; neither decomposition nor benzene formation was noted. Acetylene polymerizes[24a] under the influence of high temperatures and leads to a complex mixture of aromatic hydrocarbons, of which benzene may constitute, under some conditions, a very considerable proportion. The subject of the pyrolysis of acetylene has been discussed in Chapters 2, 4, 5 and 9, and need only be referred to briefly here. The pyrolytic process necessitates the use of temperatures of about 600° C. or higher and catalysts tend to cause the formation of methane, hydrogen, and carbon. Under such conditions benzene, derived from acetylene according to the reaction, $3C_2H_2 \rightarrow C_6H_6$, is by no means the main product and usually a whole series of aromatic hydrocarbons, both mono- and polynuclear, are simultaneously formed. According to the work of Berl and Hofmann,[25] 87 per cent of aromatic condensation products are obtained by heating acetylene at 600° to 700° C. in the presence of a beechwood charcoal contact material. With excess steam at 740° C. yields as high as 98.8 per cent were attained.

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[21] Kutscherow, *Ber.*, 1881, 14, 1540; 1884, 17, 13; Hofmann and collaborators, *Ber.*, 1898, 31, 2212, 2783; 1899, 32, 874; 1904, 37, 4459; 1905, 38, 663.

[22] Keiser, *Amer. Chem. J.*, 1893, 15, 535.

[23] Burkard and Travers, *J.C.S.*, 1902, 81, 1270.

[24] *Compt. rend.*, 1910, 150, 1169; *Chem. Soc. Abs.*, 1910, 98 (1), 349. For further work on the photochemical polymerization of acetylene, see Lind and Livingston, *J.A.C.S.*, 1932, 54, 94; *Chem. Abs.*, 1932, 26, 1193; also Livingston and Schiflett, *J. Phys. Chem.*, 1932, 36, 750; *Brit. Chem. Abs.*, A, 1932, 480; Kato, *Sci. Papers Inst. Phys.-Chem. Research* (*Tokyo*), 1931, 15, 294; *Chem. Abs.*, 1931, 25, 5845.

[24a] The polymerization and decomposition of acetylene and its homologues has been reviewed by Egloff, Lowry, and Schaad (*J. Phys. Chem.*, 1932, 36, 1457; *Chem. Abs.*, 1932, 26, 3479).

Other investigators obtained a 50 per cent yield of benzene by polymerizing acetylene at 700° C. using selenium or tellurium as a catalyst.[26] It is said that the polymerization may be carried out at 300° to 500° C. under 10 to 200 atmospheres in the presence of a heavy oil (e.g., transformer oil) and iron and magnesium bromide and yields liquids, for the most part aromatics, nearly quantitatively.[27]

Bahr [28] studied the polymerization of acetylene at moderate temperatures in the presence of various catalysts. Using ferrous sulphide a black-brown tar was formed at 300° C.; with deposition of carbon at 430° C. With 50 per cent nickel and 50 per cent tin a water-clear condensate, which later turned green or brown, was produced; carbon deposited at about 430° C. Using tinned iron turnings a small amount of liquid was produced at 250° C., but with stannous chloride and pumice no reaction was observed up to 500° C.

In the presence of zinc chloride at 420° to 430° C., Lozovoj [28a] obtained gaseous products consisting of 32 per cent acetylene, 2 per cent isoolefins, 10 per cent normal olefins, 12 per cent hydrogen, and 41 per cent saturated paraffin hydrocarbons. The unsaturated hydrocarbons identified were ethylene, propylene, 1-propinine, allene and butadiene. The liquid products contained a small proportion of olefins, benzene, toluene and naphthalene but no paraffins or naphthenes.

Fischer, Peters and Koch [28b] passed water gas containing 10 per cent acetylene over a copper-iron alkali catalyst at 250° C., 40 to 70 per cent of the acetylene being thus converted to benzine and oil. With a catalyst of copper and iron in proportions greater than 10 to 1, respectively, cuprene was formed. One per cent of nickel added to the catalyst produced 50 to 55 per cent of benzine and oil in the ratio of 3 to 1, respectively. Iron alone gave no results below 340° C., but above this temperature 35 to 40 per cent oil was formed accompanied by carbon. With cobalt, methane was quantitatively produced. Two parts of iron and 1 of nickel raised the proportion of benzine in the yield to 85 per cent, the total yield at 250° C. being 30 to 35 per cent of the acetylene used. Likewise coal gas was catalytically polymerized. One cubic meter passed first through an electric discharge and then over a heated catalyst gave 85 grams of oil, of which 75 per cent was light oil. In all cases 90 per cent of the benzine boiled between 50° and 150° C. and contained 60 per cent unsaturated compounds.

The low-temperature polymerization of acetylene has been studied very little. The action of the silent electric discharge on acetylene at low temperatures was found by Mignonac and Vanier de Saint-Aunay [29] to result in the production of dipropargyl and other highly reactive diacetylene hydrocarbons.

Nieuwland, Calcott, Downing and Carter [30] described a method of controlling the polymerization of acetylene at low temperatures by making use of the condensing action of a concentrated aqueous solution of cuprous chloride and ammonium chloride. The products consist of monovinylacetylene, divinylacetylene and a tetramer of acetylene. On introducing pure gaseous acetylene under slight pressure into a 2-liter flask containing a cooled solution of 100 grams of cuprous chloride, 390 grams of ammonium chloride, 100 grams of precipitated copper powder, 30 grams of 37 per cent hydrochloric acid, and 425 grams of water, more than 100 grams of acetylene are absorbed. During the absorption the catalyst may be allowed to warm up to 40° to 50° C. without detriment to the recovery of the products. The solution becomes light yellow in color and insoluble addition products are formed. On allowing the mixture to stand at room temperature for 5 to 7 days, polymerization of the combined or dissolved acetylene takes place. Acetylene polymers may be distilled by heating the catalyst solution to 100° to 110° C. until only water distils over. The distillate separates into two layers; the lower aqueous layer is returned to the catalyst mixture which is recharged with more acetylene; and the oily layer, consisting of a mixture of divinylacetylene and a tetramer, C_8H_8, together with small amounts of chlorine-containing products, is dried and distilled *in vacuo* on a water bath. Divinylacetylene is distilled at 200 mm. pressure and the tetramer at 20 mm., the temperature in each case being nearly 100° C. The yield of divinylacetylene is 70 to 80 per cent, and that of the tetramer 10 per cent, of the acetylene absorbed while the loss amounts to 10 to 20 per cent.[81] By a modification of the above process substantial amounts of monovinylacetylene may be obtained.

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[25] *Z. angew. Chem.*, 1931, **44**, 259; *Chem. Abs.*, 1931, **25**, 3309.

[26] Bataafsche Petroleum Maatschappij, Dutch Patent 29,094, 1933; *Chem. Abs.*, 1933, **27**, 3222.

[27] Bataafsche Petroleum Maatschappij, Dutch Patent 29,103, 1933; *Chem. Abs.*, 1933, **27**, 3222. British Patent 344,470, 1928; *Chem. Abs.*, 1932, **26**, 150.

[28] *Ges. Abhandl. Kenntnis Kohle*, **8**, 283; *Chem. Abs.*, 1930, **24**, 5717.

[28a] *J. Gen. Chem. Russ.*, 1931, **1**, 717; *Brit. Chem. Abs.* **A**, 1932, 141.

[28b] *Brennstoff-Chem.*, 1929, **10**, 383; *Chem. Abs.*, 1930, **24**, 4918; *cf.* Fischer and Peters, *Brennstoff-Chem.*, 1931, **12**, 286; *Brit. Chem. Abs.* **B**, 1931, 962; Fischer and Pichler, *Brennstoff-Chem.*, 1929, **10**, 279; *Chem. Abs.*, 1930, **24**, 483.

[29] *Compt. rend.*, 1929, **188**, 959; *Chem. Abs.*, 1929, **23**, 3437.

[30] *J.A.C.S.*, 1931, **53**, 4197.

Polymerization of acetylene under these carefully controlled conditions, therefore, leads to the formation of varying proportions of highly unsaturated hydrocarbons containing one triple bond together with one or more double bonds. The chemical and physical properties of these polymers are as follows:

Monovinylacetylene, $CH_2{=}CH{-}C{\equiv}CH$, is a colorless liquid of sweet odor, boiling point 5° C. and $d_0^t = 0.7095\text{-}0.00114\ t$. On hydrogenation it yields butadiene[82] and n-butane. Hydration of the triple bond using a catalyst (mercuric sulphate or acetate, cadmium sulphate or acetate, or silver phosphate) in sulphuric acid furnishes the unsaturated ketone, $CH_2{=}CHCOCH_3$.[83] Monovinylacetylene forms a white silver salt and a yellow copper salt with ammoniacal solutions of these metals.

On treatment with hydrochloric acid in the presence of cuprous, auric, calcium, magnesium, mercuric or mercurous chloride, monovinylacetylene gives rise to 2-chlorobutadiene, boiling point 60° C.; 2,4-dichlorobutylene, boiling point 128° C.; and chloromethylallene, boiling point 86° to 88° C.[84] Similarly with concentrated hydrobromic acid, 2-bromobutadiene, boiling point 42° to 43° C. at 165 mm.; and 2,4-dibromo-2-butene, boiling point 168° to 169° C., are produced.[85]

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[81] Nieuwland, U. S. Patent 1,811,959, June 30, 1931; assigned to E. I. duPont de Nemours & Co., Inc.; *Chem. Abs.*, 1931, **25**, 4892. See also Calcott and Downing, U. S. Patent 1,876,857, Sept. 13, 1932; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1933, **27**, 103. E. I. duPont de Nemours & Co., Inc., British Patents 384,654 and 384,655, 1931. *Brit. Chem. Abs.* **B**, 1933, 182. See also E. I. duPont de Nemours & Co., Inc., French Patents 733,663 and 733,681, 1931; *Chem. Abs.*, 1933, **27**, 1011; French Patent 41,454, 1931; addition to French Patent 733,663, 1931; *Chem. Abs.*, 1933, **27**, 2696.

[82] Calcott, Carter and Downing, U. S. Patent 1,920,242, Aug. 1, 1933; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1933, **27**, 4818. E. I. duPont de Nemours & Co., Inc., British Patent 389,108, 1933; *Chem. Abs.*, 1933, **27**, 4700.

[83] Carter, U. S. Patent 1,896,161, Feb. 7, 1933; assigned to E. I. duPont de Nemours & Co., Inc.; *Chem. Abs.*, 1933, **27**, 2458.

[84] Carothers, Williams, Collins and Kirby, *J.A.C.S.*, 1931, **53**, 4203. British Patents 387,325, 1931; *Brit. Chem. Abs.* **B**, 1933, 296. 395,131, 1932; *Brit. Chem. Abs.* **B**, 1933, 855. 389,122, 1933; *Chem. Abs.*, 1933, **27**, 4700; all assigned to E. I. duPont de Nemours & Co., Inc. Carothers, Berchet and Collins, *J.A.C.S.*, 1932, **54**, 4066. For other derivatives of vinylacetylene see Carothers and Berchet, *J.A.C.S.*, 1933, **55**, 1094; *Brit. Chem. Abs.* **A**, 1933, 485; *J.A.C.S.*, 1933, **55**, 2807; *Chem. Abs.*, 1933, **27**, 3910. *Brit. Chem. Abs.* **A**, 1933, 371.

[85] Carothers, Collins and Kirby, *J.A.C.S.*, 1933, **55**, 786.

Both 2-chlorobutadiene and 2-bromobutadiene may be polymerized to rubber-like substances.[36]

When vinylacetylene is polymerized under pressure by heating either with or without catalysts (benzoyl peroxide or sodium perborate), it forms viscous drying oils and finally hard resinous solids.[37]

Divinylacetylene, $CH_2=CH—C\equiv C—CH=CH_2$, is a colorless liquid of unusual alliaceous odor, boiling point 83.5° C. at 760 mm. and d^{20}_{4} 0.7851. As previously mentioned, it may be prepared from acetylene in the presence of an aqueous acid solution of cuprous chloride and an ammonium salt.[38] It is an extremely explosive substance and readily absorbs oxygen from the air to yield a highly explosive peroxide. Its structure is deduced from its being hydrogenated to n-hexane and brominated to a mixture of stereoisomeric, 1,2,3,4,5,6-hexabromo-3-hexenes (melting point 81° and 114° C.).

Divinyl acetylene may be partially hydrogenated to less saturated products[39]; it is said that if the partial hydrogenation is carried out under nonoxidizing conditions a more stable product is obtained.[40] The halogenation of divinylacetylene leads to products which may be used as drying oils or plastics.[41] Two substances isolated from the chlorination are 1,2,3,4,5,6-hexachlorohexene-3, and 3,4-dichlorohexatriene,1,3,5.[42]

Coffman and Carothers[42a] obtained a 25 per cent yield of 1,4-dichloro-2,3,5-hexatriene on passing chlorine into a solution of divinylacetylene in carbon tetrachloride at —56° C. for 5 hours. At —50° C. the yield was 19 per cent and at 0° C., 20 per cent. Other products consisted of a liquid dichloride and tetrachloride and a crystalline hexachloride.

By heating in an inert atmosphere, divinylacetylene may be polymerized first to a viscous liquid and finally to a hard brittle resin insoluble in all known solvents.[43] The intermediate liquid products are synthetic drying oils[44] possessing high stability but drying by oxidation and polymerization to hard films. These resinous films are stated to be highly resistant not only to solvents but also toward acids.[45] Coating compositions are also obtained from the reaction of divinylacetylene and sulphur chloride.[46]

A synthetic rubber may be obtained from emulsions of divinylacetylene or its liquid or gaseous polymers.[47] The emulsion is prepared by adding 30 parts of divinylacetylene to 100 parts of a solution containing 1 per cent gelatin and 1 per cent of sludge acids obtained in the treatment of petroleum distillates with sulphuric acid.[48] The mixture is agitated and a milky emulsion which has slight tendency to separate, results. Such an emulsion having a particle size of about 1 μ and containing a resin extracted from guayule rubber by acetone, resembles latex and on coagulation forms a synthetic rubber.

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[36] For a discussion of factors affecting rate of vulcanization of 2-chlorobutadiene polymers see Bridgwater and Krismann, *Ind. Eng. Chem.*, 1933, **25**, 280.

[37] E. I. duPont de Nemours & Co., Inc., British Patent 385,963, 1932; *Chem. Abs.*, 1933, **27**, 4252. Carter and Downing, U. S. Patent 1,896,162, Feb. 7, 1933; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1933, **27**, 2591.

[38] Nieuwland, U. S. Patent 1,811,959, June 30, 1931; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1931, **25**, 4892.

[39] E. I. duPont de Nemours & Co., Inc., British Patent 389,108, 1933; *Chem. Abs.*, 1933, **27**, 4700.

[40] Calcott, Carter and Downing, U. S. Patent 1,903,501, Apr. 11, 1933; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1933, **27**, 3222.

[41] Calcott and Carter, U. S. Patent 1,896,159, Feb. 7, 1933; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1933, **27**, 2591.

[42] E. I. duPont de Nemours & Co., Inc., British Patent 389,122, 1931; *Brit. Chem. Abs.* **B**, 1933, 540. 384,654, *Brit. Chem. Abs.* **B**, 1933, 182.

[42a] *J.A.C.S.*, 1933, **55**, 2040.

[43] Nieuwland, U. S. Patent 1,812,541, June 30, 1931; assigned to E. I. duPont de Nemours Co., Inc., *Chem. Abs.*, 1931, **25**, 5049.

[44] Collins, U. S. Patents 1,812,544 and 1,812,849, June 30, 1931; *Chem. Abs.*, 1931, **25**, 5048 and 5049.

[45] See Chilton and Huey, *Ind. Eng. Chem.*, 1932, **24**, 125.

[46] Calcott and Carter, U. S. Patent 1,896,157, Feb. 7, 1933; assigned to E. I. duPont de Nemours & Co., Inc., *Chem. Abs.*, 1933, **27**, 2591.

[47] E. I. duPont de Nemours & Co., Inc., British Patents 389,108 and 389,109, 1931; *Brit. Chem. Abs.* **B**, 1933, 540.

The so-called "tetramer," a colorless liquid resembling divinylacetylene, has d^{20} 0.830 and n^{20}_{D} 1.576. It apparently boils at 156° C. with violent decomposition and boils with polymerization at 40° C. at 20 mm., 50° C. at 30 mm., and at 82° C. at 100 mm.[49] Its probable structure is $CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH{-}CH{=}CH_2$.

The low-temperature polymerization of acetylene, therefore, results initially in the production of straight-chain highly unsaturated hydrocarbons containing one triple bond and one or more double bonds.

CUPRENE

A product of the pyrolysis of acetylene [50] is the voluminous yellow-brown solid polymer known as *cuprene* or *carbene*. This material, which appears to correspond with the formula $(CH)_x$, was first prepared by Erdman and Köthner [51] by passing acetylene over copper or copper oxide at temperatures below 250° C. Later investigations of this substance were undertaken by Alexander,[52] Gooch and Baldwin,[53] Sabatier and Senderens,[54] and especially by Kaufmann and Schneider.[55] In view of the facts that cuprene, on being heated with zinc at elevated temperatures, yielded aromatic hydrocarbons, was oxidized by fuming nitric acid to mellitic and benzoic acids, and also to naphthalene derivatives, and on bromination at 100° to 130° C. in the presence of ferric bromide furnished, among other products, hexabromohexahydrotriphenylene, it can hardly be doubted that this curious material is of aromatic nature though its precise structure is unknown.

Cuprene is now manufactured on a considerable scale but the details of the process have so far remained veiled in secrecy. It is known, however, that copper or cupriferous bronze powders have been used as catalysts at temperatures of 200° to 260° C. and under pressure, together with the combined action of dark electric discharges.[55a] A special arrangement to prevent the voluminous polymerization products from clogging up the reaction chamber is advantageous. The addition of 5 to 15 per cent of nitrogen to the acetylene has been found to yield homogeneous products of lighter color.[56] With undiluted acetylene, there is a tendency for coking to occur, resulting in the formation of dark products of lower hydrogen content. A greenish blue, neutral, strongly unsaturated tarry liquid, called "cuprene tar" is simultaneously formed in amounts of 5.5 to 7.0 per cent as well as 13 to 17 per cent of waste gases. This tar has been investigated by Schläpfer and Stadler.[57] Under proper conditions the yield of cuprene is 25 per cent. In another proposed method for the preparation of a highly adsorbent material (cuprene), acetylene at 200° to 400° C. is passed over copper, nickel.

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[48] Calcott, Downing and Powers, U. S. Patent 1,829,502, Oct. 27, 1931; assigned to E. I. duPont de Nemours & Co., Inc.

[49] Nieuwland, Calcott, Downing and Carter, *J.A.C.S.*, 1931, **53**, 4198.

[50] Other products of the pyrolysis of acetylene are described in Chapters 2, 4, 5 and 9.

[51] *Z. anorg. Chem.*, 1898, **18**, 49; *Chem. Soc. Abs.*, 1899, **76**, (1), 21.

[52] *Ber.*, 1899, **32**, 2381.

[53] *Z. anorg. Chem.*, 1899, **22**, 235. *J.S.C.I.*, 1900, **19**, 133.

[54] *Compt. rend.*, 1900, **130**, 250. *J.S.C.I.*, 1900, **19**, 230.

[55] *Ber.*, 1922, **55**, 267; Kaufmann and Mohnhaupt, *ibid.*, 1923, **56**, 2533.

[55a] Herzog, *Kunststoffe*, 1931, **21**, 49; *Chem. Abs.*, 1931, **25**, 2683. See also Brutzkus, British Patent 155,776, 1920; *Chem. Abs.*, 1921, **15**, 1585.

[56] Elektrizitätswerk Lonza A.-G., Swiss Patent 95,237, 1921; German Patent 395,549, 1922; British Patent 200,087, 1923; *Chem. Abs.*, 1924, **18**, 276; Lichtenhahn, Canadian Patent 238,888, 1924; *Chem. Abs.*, 1924, **18**, 1300.

[57] *Helv. Chim. Acta*, 1926, **9**, 185; *Chem. Abs.*, 1926, **20**, 1384.

iron, or oxides of these metals to which has been added less than 1 per cent of magnesium powder.[58]

Acetylene mixed with an indifferent gas may be conducted into stearic acid heated to 250° to 300° C. to which has been added copper bronze.[59] The cuprene made by this process is a fine powder and of a light or dark brown color. Addition of air or oxygen to the acetylene has also been proposed.[59a]

Because of its chemical inertness and its highly voluminous structure, cuprene presents industrial possibilities. Its applications as a filler in the manufacture of acid-resisting and electric insulating materials, plastic masses,[59b] electrodes and explosives, as a cork substitute [59c] in the linoleum industry and as an adsorbing agent for illuminants and fuels or volatile substances [59d] have been discussed by Herzog.[60] Sulphurized cuprene, containing 11 per cent of sulphur, is prepared by refluxing cuprene with sulphur monochloride in the presence of benzene. When working under 10 atmospheres pressure at 180° to 200° C. a product containing 13.6 per cent of sulphur and 4 per cent of chlorine is obtained which may be employed in the rubber industry.

HALOGEN DERIVATIVES OF ACETYLENE

A number of halogen derivatives of both substitution, addition, and substituted-addition types are known and some of these products, especially those containing chlorine, are of industrial importance. Only the chlorine derivatives will be considered in the following brief account.[60a]

Though chlorine is without action on pure acetylene in the dark, addition occurs smoothly in diffused daylight with the ultimate formation of the tetrachloride $C_2H_2Cl_4$, the dichloride being an intermediate product. In practice, however, direct combination of acetylene and chlorine to yield the tetrachloride may be accompanied by violent explosions, particularly in presence of traces of impurities. For this reason, catalysts are often employed to control the reaction. If desired, however, the reaction can be stopped at the intermediate dichloride stage by adjustment of operating conditions.[61] Thus, trans-1,2-dichloroethylene is the main product when a mixture of chlorine and excess of acetylene is led at high space velocities over active carbon at temperatures below 100° C., the optimum temperature being about 40° C.[62]

Acetylene tetrachloride (tetrachloroethane, $Cl_2HCCHCl_2$) is by far the most important of the industrial halogen derivatives of acetylene and serves as a starting material for the synthesis of a number of solvents, notably of trichloroethylene and its derivatives. As previously stated, it is prepared by the direct combination of acetylene and chlorine in the presence of catalysts, which serve to obviate the danger of explosions. A number of catalysts have been proposed including iodine monochloride,[63] aluminum chloride,[64] ferric chloride,[65] iron filings and bone charcoal,[66] and antimony pentachloride,[67] but the last substance appears to be most generally employed.[67a] The reacting gases are introduced either simultaneously or alternately into a solution of antimony pentachloride in acetylene tetrachloride at a slightly elevated temperature. According to Igi,[68] the optimum temperature for absorption in antimony pentachloride is 80° to 100° C.[68a] for chlorine and 60° to 80° C. for acetylene. In the preparation of acetylene tetrachloride the acetylene is passed in first at the lower temperature. Various intermediate compounds such as antimony chloroacetylide and antimony trichloride are probably formed. Acetylene tetrachloride has been formed in 93 per cent yield by passing 1 volume of acetylene and 2 volumes of chlorine through a tube at 205° C. carrying a water-cooled tube at 110° C.[68b] Fukagawa [69] states that an iron-silicon-aluminum alloy is a catalyst.

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[58] Liefde, U. S. Patent 1,828,560, Oct. 20, 1931; *Chem. Abs.*, 1932, **26**, 814; British Patent 303,797, 1929; *Brit. Chem. Abs.* **B**, 1930, 705; German Patent 534,118, 1929; *Chem. Abs.*, 1932, **26**, 735; all patents assigned to N.-V. Electro Zuurstofen, Waterstoffabriek.

[59] Elektrizitätswerk Lonza, German Patent 407,485, 1922; *J.S.C.I.*, 1925, **44**, 475B.

[59a] Horwitz, German Patent 205,705, 1907; Chem. Abs., 1909, **3**, 1925.

[59b] Kühn, U. S. Patent 1,522,822, Jan. 13, 1925; *Chem. Abs.*, 1925, **19**, 909; British Patent 192,080, 1923; *Chem. Abs.*, 1923, **17**, 3429; German Patent 455,551, 1923; *Chem. Abs.*, 1923, **17**, 3429; all patents assigned to Elektrizitätswerk Lonza A.-G. Sinit A.-G., German Patent 455,551, 1923; *Brit. Chem. Abs.* **B**, 1930, 157.

[59c] Sulser, U. S. Patent 1,511,784, Oct. 14, 1924; *Chem. Abs.*, 1925, **19**, 186. Elektrizitätswerk Lonza A.-G., British Patent 189,146, 1922; *Chem. Abs.*, 1923, **17**, 2482; Swiss Patent 102,757, 1923; *Kunststoffe*, 1925, **15**, 45; German Patent 395,706, 1921; *Kunststoffe*, 1925, **15**, 122.

[59d] Lepsius, German Patent 396,289, 1921; *J.S.C.I.*, 1924, **43**, 818B.

[60] *Kunststoffe*, 1931. **21**, 49; *Chem. Abs.*, 1931, **25**, 2683; *Chem. Umschau*, 1931, **35**, 675; *Chem.-Ztg.*, 1931, **55**, 461. The possible use of cuprene as an adsorbent for nitroglycerin or liquid oxygen is discussed by Foulon, *Z. ges. Schiess-Sprengstoffw.*, 1932, **27**, 48; *Chem. Abs.*, 1932, **26**, 2596.

[60a] The reaction of acetylene with iodine in liquid ammonia and the direct iodination of monosubstituted acetylenes has been investigated by Vaughn and Nieuwland (*J.A.C.S.*, 1932, **54**, 787; *ibid.*, 1933, **55**, 2150). Van de Walle and de Landsberg (*Bull. acad. roy. Belg.*, 1930, (5) **16**, 369; *Brit. Chem. Abs.* **A**, 1930, 1018) prepared s-bromoiodoethylene from acetylene and a mixture of bromine and iodine.

[61] The chlorination of acetylene has been reviewed by Valyashko and Kosenko. *Ukrain. Khem. Zhur.*, 1932, **7**, No. 1, 12; *Chem. Abs.*, 1933, **27**, 1611; *Brit. Chem. Abs.* **A**, 1933, 47.

[62] Ruppert, Fischer, Voigt and Hennig, U. S. Patent 1,868,077, July 19, 1932; *Chem. Abs.*, 1932, **26**, 5106; German Patent 553,149, 1922; *Chem. Abs.*, 1933, **27**, 736; British Patent 310,964, 1929; *Brit. Chem. Abs.* **B**, 1930, 807; all patents assigned to I. G. Farbenindustrie A.-G.

Acetylene tetrachloride is a colorless liquid of boiling point 145.5° C. and d_4^{15} 1.6011. It is a solvent for fats, varnishes and cellulose acetate, but its use has been greatly restricted by its very marked toxic properties and its ease of decomposition in the presence of moisture. As a solvent, it has been largely displaced by a number of its derivatives which are equally satisfactory for most purposes, are much less toxic, and exhibit greater stability.[69a] One of the most important of these derivatives is the substance trichloroethylene, $CHCl{=}CCl_2$. This is manufactured on a large scale by heating acetylene tetrachloride with an alkali, such as lime [70] or ammonia,[71] whereby an almost theoretical yield is obtained. MacMillan [72] prepares trichloroethylene by heating acetylene tetrachloride with lime, water, and sodium carbonate at about 100° C. Guyot [73] prefers aqueous ammonia at 140° to 170° C. as the dechlorinating agent. Other proposed methods of converting acetylene tetrachloride into trichloroethylene include the catalytic decomposition of the former substance in the presence of heated copper or barium chlorides [74] or of thorium dioxide at 390° C.[75] Trichloroethylene may also be obtained by passing acetylene tetrachloride vapor mixed with steam or xylene vapor over a catalyst at 450° to 500° C.[75a] The catalyst is prepared by shaking moistened pumice with finely powdered copper phosphate.

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[63] Sabanejev, *Ann.*, 1883, **216**, 241, 251; *Chem. Zentr.*, 1883, 482.

[64] Mouneyrat, *Compt. rend.*, 1898, **126**, 1805; *Chem. Soc. Abs.*, 1898, **74** (1), 613; *Bull. soc. chim.*, 1898, (3) **19**, 448.

[65] Ornstein, British Patent 2375, 1911; *J.S.C.I.*, 1911, **30**, 982; French Patent 420,489, 1910; *J.S.C.I.*, 1911, **30**, 307; Hoefer and Mugdan, U. S. Patent 985,528, Feb. 28, 1911; *J.S.C.I.*, 1911, **30**, 446; Consortium für elektrochemische Industrie G.m.b.H., British Patent 25,967, 1910; French Patent 425,327, 1910; *J.S.C.I.*, 1911, **30**, 923.

[66] Tako, Japanese Patent 90,708, 1931; *Chem. Abs.*, 1931, **25**, 4894.

[67] Berthelot and Jungfleisch, *Ann.*, 1870, **7**, 252; Askenasy and Mugdan, British Patent 18,602, 1904, *J.S.C.I.*, 1905, **24**, 150. Tompkins, British Patent 19,568, 1904, *J.S.C.I.*, 1905, **24**, 902. Dreyfus and Tompkins, British Patent 8438, 1909, assigned to Clayton Aniline Co.; *J.S.C.I.*, 1910, **29**, 81.

[67a] For the chlorination of acetylene mixed with other gases see Ruhrchemie A.-G., French Patent 743,778, 1933; *Chem. Abs.*, 1933, **27**, 3941.

[68] *J. Soc. Chem. Ind.* (*Japan*), 1920, **23**, 1217; *Chem. Abs.*, 1921, **15**, 2273; *cf.* Kraft and Alekseyev, *J. Chem. Ind. Russia*, 1931, **8**, 861; *Chem. Abs.*, 1932, **26**, 79.

[68a] I. G. Farbenindustrie A.-G. (French Patent 739,183, 1932; *Chem. Abs.*, 1933, **27**, 1894) suggests a temperature of 80° to 146° C. for the treatment of acetylene with chlorine.

[68b] Ruhrchemie A.-G., British Patents 378,873, and 378,979, 1931; *Brit. Chem. Abs.* **B**, 1932, 1071.

[69] *Proc. World Eng. Congr.*, 1929, **31**, 387; *Brit. Chem. Abs.* **B**, 1931, 796.

[69a] The stability of trichloroethylene has been investigated by Carlisle and Levine, *Ind. Eng. Chem.*, 1932, **24**, 1164.

[70] Consortium für elektrochemische Industrie, German Patent 171,900, 1905, and 208,834, 1907; *J.S.C.I.*, 1907, **26**, 279; *Chem. Abs.*, 1909, **3**, 2210.

[71] Tompkins, British Patent 19,568, 1904.

[72] U. S. Patent 1,397,134, Nov. 11, 1921; *Chem. Abs.*, 1922, **16**, 565.

[73] Canadian Patent 213,788, 1921; *Chem. Abs.*, 1922, **16**, 1099.

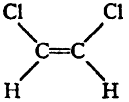
[74] Chem. Fabrik Griesheim Elektron, German Patent 263,457, 1912; *Chem. Abs.*, 1913, **7**, 4048.

[75] Chem. Fabrik Bückau, German Patent 274,782, 1912; *Chem. Abs.*, 1914, **8**, 3350.

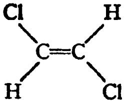
Trichloroethylene is a colorless liquid of boiling point 87° C. at 760 mm. and d^{15}_{4} 1.471, possessing solvent power[76] for fats, waxes, resins, rubber and other organic compounds as well as for sulphur and phosphorus. It is utilized in the extraction of fats and in dry cleaning[76a] and as a dehydrating agent (by azeotropic distillation) in the production of absolute alcohol.[76b] It may be used as a raw material for the production of pentachloroethane,[76c] dichloroethylene, dichlorovinyl ether, chloroacetic acid, and glycollic acid. According to Dangelmajer,[77] 10 per cent of an aliphatic petroleum fraction of boiling range 40° to 232° C. stabilizes trichloroethylene. Hexylresorcinol[77a] has also been suggested for this purpose.

1,2-Dichloroethylene, or acetylene dichloride, exists in two geometrically isomeric forms,

(*cis*)



(*trans*)



which have the following physical properties:

	cis-Dichloroethylene	trans-Dichloroethylene
b.p. ° C. at 760 mm.	59.8°	48.8°
m.p. ° C.	—80.5°	—50°
d^{15}_{4}	1.289	1.265

These isomeric compounds may be produced from acetylene tetrachloride by heating with water and zinc at 100° C. or with iron and water at 150° to 200° C. in an autoclave.[77b] A vapor-phase process in which the mixed vapors of the tetrachloride and steam are passed over a heated iron catalyst at ordinary pressure, has also been described.[78] Dichloroethylene is said to be produced when 1,1,2-trichloroethane[78a] is passed at about 500° C. over a heated surface which is coated with a salt of copper, iron or an alkaline earth metal.[79] It may also be

[75a] Schering-Kahlbaum A.-G., British Patent 374,949, 1932; *Chem. Abs.*, 1933, **27**, 3951.

[76] The use of trichloroethylene in solvent extraction is discussed by MacGregor, *Chem. Age*, 1931, **25**, 576. Backlund (*J. Inst. Pet. Tech.*, 1933, **19**, 1; *Brit. Chem. Abs.* **B**, 1933, 292) describes its application in dewaxing petroleum oils. The use of trichloroethylene as a degreasing agent was described by Robertson (U. S. Patent 1,905,968, April 25, 1933; *Chem. Abs.*, 1933, **27**, 3437; U. S. Patent 1,907,875, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3761; both patents assigned to Carrier Engineering Co., Ltd. *Cf.* also Reid, *Ind. Eng. Chem.*, 1934, **26**, 21).

[76a] See Brown, *Dyer*, 1932, **68**, 79; *Chem. Abs.*, 1932, **26**, 5425; *cf.* Bird, *Dyer*, 1932, **68**, 185; *Chem. Abs.*, 1932, **26**, 5426.

[76b] Fritzweiler and Dietrich, *Internat. Sugar J.*, 1933, **35**, 29, 71; *Brit. Chem. Abs.* **B**, 1933, 327.

[76c] Pentachloroethane may also be prepared by the exhaustive chlorination of 1, 1-dichloroethylene (I. G. Farbenindustrie A.-G., German Patent 530,649, 1929; *Chem. Abs.*, 1932, **26**, 155).

[77] U. S. Patent 1,816,895, Aug. 4, 1931; *Brit. Chem. Abs.* **B**, 1933, 216; Canadian Patent 303,663, 1930; both patents assigned to Roessler and Hasslacher Chemical Co.

[77a] Pitman, U. S. Patent 1,910,962, May 23, 1933; assigned to Westvaco Chlorine Products, Inc., *Chem. Abs.*, 1933, **27**, 3951.

[77b] Consortium für elektrochemische Industrie G.m.b.H., German Patent 216,070, 1907; *Chem. Zentr.*, 1909, **2**, 2103; German Patent 217,554, 1907; *Chem. Zentr.*, 1910, **1**, 700.

[78] Wacker Gesellschaft für Elektrochemische Ind., British Patent 156,080, 1920; *Chem. Abs.*, 1921, **15**, 1535.

[78a] For the manufacture of 1,1,2-trichloroethane see I. G. Farbenindustrie A.-G., British Patent 344,592, 1929; *Chem. Abs.*, 1932, **26**, 155.

[79] Herrmann and Baum, U. S. Patent 1,921,879, Aug. 8, 1933; *Chem. Abs.*, 1933, **27**, 5086; British Patent 348,346, 1929; *Chem. Abs.*, 1932, **26**, 5106; German Patent 570,954, 1933; *Chem. Abs.*, 1933, **27**, 4252; all patents assigned to Consortium für elektrochemische Industrie, G.m.b.H.

made directly from acetylene and chlorine[80]; various catalysts, cupric chloride,[81] activated carbon,[82] nickel deposited on active carbon[83] and silica gel[83a] have been suggested.

Dichloroethylene resembles trichloroethylene in chemical properties. It is said to be a good solvent for rubber,[84] and the lower boiling form has been proposed as a refrigerant for ice machines.[85] Clarke and Othmer[85a] suggested the application of dichloroethylene for the removal of water from acetic acid. Its use for the manufacture of chloroacetyl chloride has been proposed.[86] When hydrogen chloride is passed into a mixture of 1,1,2-trichloroethylene and aluminum chloride at 50° C., pentachlorobutadienes, hexachlorobenzene, 1,1,2,2- and 1,1,1,2-tetrachloroethane in proportions of 1 to 5, are obtained.[86a] Similarly, dichloroethylene yields 1,1,2-trichloroethane and a pentachlorobutane.

Asymmetrical-dichloroethylene is formed[87] when 1,1,1- or 1.1,2-trichloroethane is slowly heated to 70° to 80° C. with excess of lime; the yield of 1,1-dichloroethylene is approximately 90 per cent.

Mono- and dichloroacetylene are highly unstable, volatile liquids which as yet have no industrial applications. The manufacture of dihalogen substituted acetylenes may be carried out by passing acetylene into an ice-cooled alkaline solution of a hypochlorite or hypobromite.[88] In this way, dichloroacetylene and dibromoacetylene,

$ClC{\equiv}CCl$ and $BrC{\equiv}CBr$
b.p. + 32° C. b.p. 76°-77° C.
m.p. −64° to −68° C.

may be obtained very readily. Acetylene and bromine combined to the extent of 60 per cent when passed over pumice at 160° to 170° C.[88a] The product consisted of a mixture of halogenated compounds, from which a separation of dibromoethylene is complicated. The melting point determination indicated a yield of 29 per cent ethylene bromide although the viscosity indicated a yield of 45 per cent.

THE HYDRATION OF ACETYLENE TO ACETALDEHYDE

The direct hydration of acetylene to yield acetaldehyde according to the equation $C_2H_2 + H_2O \rightarrow CH_3CHO$, is perhaps the most important of the chemical reactions of that hydrocarbon. Acetaldehyde is a widely used chemical intermediate and is utilized in the production of n-butanol, acetic acid, ethyl acetate, and numerous other products. On reduction with hydrogen in the presence of a catalyst, acetaldehyde yields ethanol so that the synthesis of that alcohol from acetylene is readily accomplished.

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[80] Chem. Fabrik Griesheim Elektron, German Patent 254,069, 1911; *Chem. Abs.*, 1913, **7**, 869. I. G. Farbenindustrie A.-G., British Patent 310,964, 1928; *Chem. Abs.*, 1930, **24**, 630.

[81] Consortium für Elektrochemische Industrie G.m.b.H. British Patent 366,348, 1930; *Brit. Chem. Abs.* **B**, 1932, 493. French Patent 714,995, 1931; *Chem. Abs.*, 1932, **26**, 1624.

[82] Ruppert, Fischer, Voigt and Hennig, U. S. Patent 1,868,077. July 19, 1932; assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1932, **26**, 5106.

[83] Wiegand, German Patent 566,034, 1931; assigned to Chem. Fab. von Heyden A.-G.; *Chem. Abs.*, 1933, **27**, 1011.

[83a] Compagnie de produits chim. et electrométallurgiques Alais, Froges et Camargue, French Patent 744,359, 1933; *Chem. Abs.*, 1933, **27**, 3951.

[84] Fischer, German Patent 211,186, 1907; *Chem. Abs.*, 1909, **3**, 2633.

[85] Carrier, British Patent 237,949, 1924; assigned to Carrier Engineering Co., Ltd.; *Chem. Abs.*, 1926, **20**, 1876.

[85a] U. S. Patent 1,804,745, April 12, 1931; assigned to Eastman Kodak Co., *Brit. Chem. Abs.* **B**, 1932, 94.

[86] Chem. Fabrik Weiler-ter Meer, German Patent 363,744, 1921.

[86a] Müller and Hönn, *J. pr. Chem.*, 1932, (2) **133**, 289; *Brit. Chem. Abs.* **A**, 1932, 717.

[87] I. G. Farbenindustrie A.-G., British Patent 349,872, 1930; *Brit. Chem. Abs.* **B**, 1931, 917; German Patent 529,604, 1929; *Chem. Abs.*, 1931, **25**, 5178.

[88] I. G. Farbenindustrie A.-G., British Patent 333,946, 1930; *Brit. Chem. Abs.* **B**, 1930, 1015.

[88a] De Carli, *Ann. chim. applicata*, 1932, **22**, 455; *Chem. Abs.*, 1932, **26**, 5904.

The direct hydration of acetylene to acetaldehyde is an exothermic reaction which can be conducted in either the liquid or the gaseous phase. On an industrial scale the hydration is effected by passing a stream of acetylene through dilute sulphuric acid in the presence of a catalyst. The catalyst usually consists of a mercuric salt, such as mercuric sulphate, dissolved in the acid. It is beyond the scope of this work to discuss in detail the voluminous literature of the subject. One process,[89] however, for the conversion of acetylene into acetaldehyde is as follows: A vigorous current of acetylene, about 60 cubic feet per minute, is passed through a well-agitated liquid bath consisting of 1000 gallons of 6 per cent sulphuric acid, to which has been added 23 pounds of mercuric oxide. The reaction proceeds at ordinary pressure with heat evolution so that cooling may be necessary to control the temperature which is kept at 60°-65° C. The excess acetylene carries away the acetaldehyde produced, which is recovered by cooling the exit gases, and rectifying. Owing to a slow but continuous reduction of the mercuric salt to metallic mercury it is necessary to add fresh mercuric oxide from time to time. The metallic mercury is reoxidized electrolytically. The yield of acetaldehyde is as high as 98 per cent of the acetylene consumed. Other processes use more concentrated sulphuric acid (15 to 25 per cent) at 65° to 80° C. It is said that the reduction of the catalytic mercuric salts to mercury may be inhibited by the addition of oxidants, such as ferric salts or chromic acid.[90]

Attention has been directed toward the vapor-phase catalytic hydration of acetylene. At temperatures up to about 350° C. the thermodynamic tendency appears to be for the hydration process to proceed almost completely. One of the obvious difficulties of such vapor-phase processes is the extraordinary reactivity of acetaldehyde itself in the presence of numerous contact materials, rendering it very liable to be converted into crotonaldehyde or esters. Several procedures have been developed by Horsley[91] for the vapor-phase hydration of acetylene, such as by passing this hydrocarbon admixed with an excess of steam over (1) zinc oxide activated with molybdic acid or a molybdate at 325° C., (2) a compound of bismuth at 200° to 350° C., (3) cadmium metaphosphate at 300° to 400° C. at high space velocities, and (4) a compound of boron trioxide and phosphoric acid at 200° to 400° C. When using cadmium metaphosphate there is a tendency for crotonaldehyde to be produced, and the amount of this compound formed is dependent upon the proportions of cadmium oxide and phosphoric oxide in the catalyst. Catalysts used by other investigators are, anhydrous aluminum oxide activated with heavy metals of groups I or VIII of the periodic table,[92] anhydrous oxides, sulphides or carbides of tungsten,[93] zinc chloride,[94] and various phosphate catalysts.[94a]

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[89] Matheson, British Patents 132,557, 132,559 and 132,560, 1918; assigned to Canadian Electrochemical Products Co.; *J.S.C.I.*, 1919, **38**, 819A, 845A. The industrial preparation of acetaldehyde also is described by Cadenhead (*Chem. Met. Eng.*, 1933, **40**, 184). Benson and Cadenhead (*J.S.C.I.*, 1934, **53**, 40T) described a large number of by-products which form in minute amounts in the large-scale synthesis of compounds from acetylene.

[90] Duden and Peters, U. S. Patents 1,151,928 and 1,151,929, Aug. 31, 1915; *J.S.C.I.*, 1915, **34**, 1031; German Patent 292,818, 1914; *Chem. Abs.*, 1917, **11**, 1518; German Patent 293,070, 1914; *J.S.C.I.*, 1916, **35**, 1082; all patents assigned to Farbwerke vorm. Meister, Lucius und Brüning. Consortium für elektrochemische Industrie G.m.b.H., German Patents 309,103 and 309,104, 1916; *J.S.C.I.*, 1920, **39**, 427A.

[91] British Patent 334,427, 1929; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 972. Tanner, British Patent 344.638, 1930; to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1931, **25**, 4559; British Patent 351,016, 1930, *Chem. Abs.*, 1932, **26**, 2990. Horsley, British Patent 351,016, 1930; *Brit. Chem. Abs.* **B**, 1931, 1003. British Patent 346,288, 1930; *Chem. Abs.*, 1932, **26**, 479; both patents assigned to Imperial Chemical Industries, Ltd.

[92] Zobel and Luther, German Patent 568,547, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2696.

Closely related to the hydration of acetylene to acetaldehyde are the various processes advanced for the direct synthesis of acetic acid, metal acetates and acetone[94b] from acetylene.[94c] The formation of acetic acid probably follows that of acetaldehyde by oxidation and acetone may be synthesized from acetic acid according to the reaction:

$$2CH_3COOH \longrightarrow (CH_3)_2CO + H_2O + CO_2$$

Alkali metal acetates are produced from acetylene in alkaline solution and the reaction is said to proceed as follows:

$$NaOH + C_2H_2 + H_2O = CH_3COONa + H_2$$

Acetic acid and acetaldehyde may be made by conducting acetylene, saturated with steam at 100° to 200° C. with added oxygen over a mercury catalyst, e.g., mercuric orthophosphate or mercuric vanadate, or a mixture of mercuric sulphate and silver or tin vanadate.[95] In another procedure, a mixture of acetylene, steam and oxygen is first passed through mercury heated to 300° C. and then over a hydration catalyst which may be mercuric phosphate mixed with heavy metal salts or oxides.[96] Nitrogen oxides have also been used in the synthesis of acetic acid from acetylene presumably to catalyze the oxidation of acetaldehyde to acetic acid.[97] Still another method calls for the passage of an acetylene-steam mixture through molten zinc chloride at 300° to 450° C.[98] Catalysts, such as barium sulphate and zinc oxide or a mixture of zinc oxide, chromium oxide, barium oxide and potassium hydroxide may be used.

Acetone may be synthesized by passing acetylene and steam at 350° to 500° C. over zinc oxide.[99] Other catalysts are manganese dioxide and manganese acetate,[100] ferric oxide[101] or heavy metal oxides.[102] An 89 per cent yield of acetone is formed when a mixture of acetylene, steam and ethyl alcohol vapor is passed at 470° C. over a catalyst consisting of oxidized iron sponge containing 3 per cent of manganese dioxide.[102a] Dreyfus[102b] forms aliphatic ketones from acetylene and steam by using a catalyst prepared by heating a mixture of one or more alkaline earth oxides and one or more oxides of heavy metals or silicon dioxide.

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[93] Dietrich and Wietzel, German Patent 544,286, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2471. See also I. G. Farbenindustrie A.-G., French Patent 717,184, 1931; *Chem. Abs.*, 1932, **26**, 2752.

[94] I. G. Farbenindustrie A.-G., British Patent 393,690, 1932; *Brit. Chem. Abs.* **B**, 1933, 822. See also Müller and Lübke, German Patent 575,533, 1933; assigned to Boehringer and Soehne G.m.b.H. *Chem. Abs.*, 1933, **27**, 4819.

[94a] Andrussov and Dürr, U. S. Patent 1,882,712, Oct. 18, 1932; *Chem. Abs.*, 1933, **27**, 736; German Patent 550,933, 1930; *Chem. Abs.*, 1932, **26**, 4924; both patents assigned to I. G. Farbenindustrie A.-G.

[94b] These methods for the production of acetone should be compared with those described in Chapter 18.

[94c] The oxidation of acetaldehyde to acetic acid is discussed also in Chapter 38.

[95] Jochheim, U. S. Patent 1,828,372, Oct. 20, 1931; *Chem. Abs.*, 1932, **26**, 737. German Patent 533,466, 1927, *Chem. Abs.*, 1932, **26**, 480; both patents assigned to I. G. Farbenindustrie A.-G. I. G. Farbenindustrie A.-G., British Patent 321,241, 1928; *Chem. Abs.*, 1930, **24**, 2474.

[96] Eberhardt, German Patent 554,784, 1930, assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1932, **26**, 5971. I. G. Farbenindustrie, British Patent 364,255, 1932; *Chem. Age (London)*, 1932, **26**, 358.

[97] Gutehoffnungshütte Oberhausen A.-G., British Patent 376,045, 1931; *Brit. Chem. Abs.* **B**, 1932, 972.

[98] Consortium für Elektrochemische Industrie G.m.b.H. French Patent 722,190, 1931; *Chem. Abs.*, 1932, **26**, 4067. British Patent 373,893, 1931; *Brit. Chem. Abs.* **B**, 1932, 832.

[99] Schlecht, U. S. Patent 1,910,815, May 23, 1933; assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1933, **27**, 3951. *Cf.* Walter and Schulz, U. S. Patent 1,892,742, Jan. 3, 1933; assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1933, **27**, 2163.

[100] Róka, German Patent 566,833, 1929; *Chem. Abs.*, 1933, **27**, 2459; *cf.* Pohl, German Patent 567, 118, 1930; *Chem. Abs.*, 1933, **27**, 1365; both patents assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler. See also Nippon Chissohiryo K. K., British Patent 359,878, 1930; *Chem. Abs.*, 1933, **27**, 311.

[101] Róka and Wiesler, German Patent 565,944, 1926; assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1933, **27**, 2459.

[102] Soc. industrielle des derivés de l'acétylène, French Patent 712,967, 1931; *Chem. Abs.*, 1932, **26**, 1624; Holzverkohlungs-Industrie A.-G., British Patents 344,449 and 347,695, 1929; *Chem. Abs.*, 1932, **26**, 156, 1624.

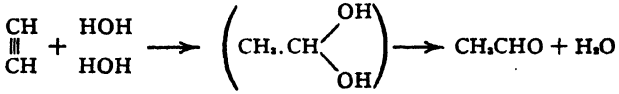
Strosacker and Stephenson[103] produce sodium acetate from acetylene by continuously supplying acetylene and steam at a temperature above 200° C. to a mixture of pulverized sodium hydroxide and sodium acetate. Mugdan and Wimmer[104] lead acetylene and steam above 200° C. through a melt of alkali hydroxide. The melting point of the hydroxide is reduced by addition of alkali acetate or water. Vinyl chloride can be reacted similarly with sodium hydroxide at 100° to 500° C. under pressure to form sodium acetate, according to Strosacker and Pelton.[104a]

Alkali metal acetylides are made by treating molten metals with acetylene.[104b] The fused metal may be diluted with an inert solid diluent such as sodium chloride.

CONDENSATION OF ACETYLENE WITH HYDROXY-COMPOUNDS

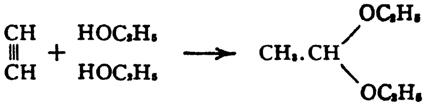
Acetylene may be condensed with alcohols, and hydroxy-compounds, in the presence of catalysts, to furnish di-ethers of the hypothetical ethylidene glycol (acetals). The reaction is strictly analogous to the addition of water to acetylene, which may be assumed to proceed through the intermediate formation of ethylidene glycol, the hydrated form of acetaldehyde. The analogy is illustrated by the following reactions:

(1) *With water:*



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + \begin{matrix}HOH\\ \\ HOH\end{matrix} \longrightarrow \left(CH_3.CH\begin{matrix}OH\\ \\ OH\end{matrix}\right) \longrightarrow CH_3CHO + H_2O$$

(2) *With ethanol:*



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + \begin{matrix}HOC_2H_5\\ \\ HOC_2H_5\end{matrix} \longrightarrow CH_3.CH\begin{matrix}OC_2H_5\\ \\ OC_2H_5\end{matrix}$$

diethyl acetal

Acetals may be conveniently prepared by passing acetylene into an alcohol, such as ethanol, in the presence of a mercuric salt.[105] The reaction is not limited to simple aliphatic monohydric alcohols and appears to possess commercial possibilities. For example, the acetal of the monoethyl ether of diethylene glycol can be made by leading acetylene into an ethanol solution of that ether in the presence of mercuric oxide and fluoboric acid.[106]

It may be noted that the combination of alcohols with acetylene probably proceeds with the intermediate formation of vinyl ethers of the general type $CH_2{=}CHOC_nH_{2n+1}$, which then combine with another molecule of alcohol. Vinyl ethers may be condensed with alcohols to yield acetals in the presence of a trace of sulphuric acid at temperatures not above 30° C.[107]

[102a] Holzverkohlungs-Industrie A.-G., British Patent 344,449, 1929; *Brit. Chem. Abs.* **B**, 1931, 620.

[102b] French Patent 713,845, 1931; *Chem. Abs.*, 1932, **26**, 1616.

[103] U. S. Patent 1,866,328, July 5, 1932; *Chem. Abs.*, 1932, **26**, 4345. Strosacker, Kennedy and Pelton, U. S. Patent 1,866,329, July 5, 1932; *Chem. Abs.*, 1932, **26**, 4345. U. S. Patent 1,866,430, July 5, 1932; *Chem. Abs.*, 1932, **26**, 4345. All patents assigned to Dow Chemical Co. Also Dow Chemical Co., British Patent 363,948, 1931; *Brit. Chem. Abs.* **B**, 1932, 260.

[104] German Patent 540,207, 1930 assigned to Consortium für Elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, **26**, 1621.

[104a] U. S. Patent 1,884,354, Oct. 25, 1932; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 1006.

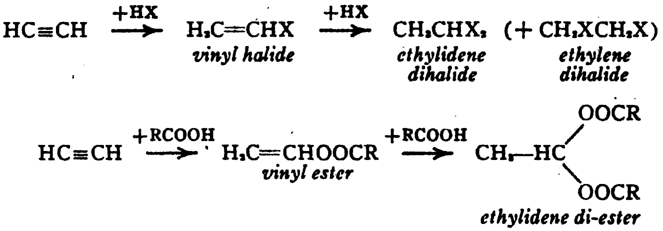
[104b] Schulenberg, German Patent 535,071, 1930; *Chem. Abs.*, 1932, **26**, 1297; German Patent 539,573, 1930; *Chem. Abs.*, 1932, **26**, 1944; French Patent 689,466, 1930; *Chem. Abs.*, 1931, **25**, 909; all patents assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler.

[105] Chem. Fabrik Griesheim Elektron, British Patent 14,246, 1913; *J.S.C.I.*, 1914, **33**, 767. Boiteau, British Patent 15,806, 1914; *Chem. Abs.*, 1916, **10**, 93. Boiteau, British Patent 15,919, 1914; *Chem. Abs.*, 1916, **10**, 93.

[106] Nieuwland, U. S. Patent 1,824,963, Sept. 29, 1931; *Chem. Abs.*, 1932, **26**, 151; U. S. Patent 1,907,560, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3486; British Patent 384,332, 1932; *Chem. Abs.*, 1933, **27**, 4252; all patents assigned to E. I. duPont de Nemours & Co.

Condensation of Acetylene with Hydrogen Halides and Organic Acids

Both halogen acids and organic acids may be condensed with acetylene with the addition first of one and then of two molecules of acid to the hydrocarbon molecule. The first stage in the reaction gives rise to vinyl esters, and the second step, to ethylidene di-esters. In the case of the halogen acids it appears that though addition usually takes place in such a way that ethylidene derivatives are formed predominantly, under certain conditions, particularly in the case of hydrogen bromide, a certain amount of ethylene dihalides are also obtained.[108] On the other hand, addition of two molecules of an organic acid to the acetylene molecule seems to produce only ethylidene di-esters. These reactions are represented by the following scheme:



$$HC{\equiv}CH \xrightarrow{+HX} \underset{\textit{vinyl halide}}{H_2C{=}CHX} \xrightarrow{+HX} \underset{\textit{ethylidene dihalide}}{CH_3CHX_2} \quad (+\ \underset{\textit{ethylene dihalide}}{CH_2XCH_2X})$$

$$HC{\equiv}CH \xrightarrow{+RCOOH} \underset{\textit{vinyl ester}}{H_2C{=}CHOOCR} \xrightarrow{+RCOOH} \underset{\textit{ethylidene di-ester}}{CH_3{-}HC\begin{matrix} \diagup OOCR \\ \diagdown OOCR \end{matrix}}$$

It is interesting to note that the interaction of acetylene with fuming sulphuric acid mainly results in the production of acetaldehydedisulphonic acid[109] of the formula $(SO_3H)_2CHCHO$. Atterbury and Macalpine[110] produced ethyl alcohol by passing equal volumes of acetylene and hydrogen into hot concentrated sulphuric acid and then diluting the acid with water. Vinylsulphuric acid is said to be formed by forcing acetylene under pressure into concentrated sulphuric acid containing mercuric sulphate at temperatures below 0° C.[111]

Vinyl Esters. The vinyl esters are remarkable for their ease of polymerization to amorphous and resinous substances under the influence of heat, actinic light or oxidizing agents. Under proper conditions clear and colorless masses, either non-inflammable or difficultly so, may be obtained which can be molded and machined. The industrial application of these resinous polymers of vinyl esters has been hindered mainly by the absence of economical methods of manufacturing such esters. The esters which have been suggested for the production of resinous materials are the *chloride, acetate,* and *chloroacetates.*[112]

Vinyl halides may be obtained by the action of concentrated aqueous hydrogen halides on calcium carbide at 60° to 95° C. in the presence of a catalyst consisting, for example, of a mixture of mercury and copper salts. However, the catalytic vapor-phase combination of dry hydrogen halides with acetylene appears to be the most convenient mode for the production of these halides. It has been reported that vinyl chloride may be obtained in quantitative yield by passing a mixture of hydrogen chloride and acetylene at 180° C. over a contact mass of pumice impregnated with mercuric chloride.[113] Vinyl halides can also be made by vapor-phase combination at elevated temperatures in the presence of compounds of elements of groups II and V of the periodic system or of mixtures of such compounds.[114] In another process the catalyst for vapor-phase combination of hydrogen halides and acetylene at 100° to 300° C. is carbon which has been previously activated by preheating in the presence of the hydrogen halide at a higher temperature (200° to 600° C.) than that used for reaction.[115] The production of vinyl chloride from acetylene and hydrochloric acid is said by Nieuwland[116] and also by Perkins[117] to proceed in the presence of a mixture of cuprous chloride and ammonium chloride. Acetylene and hydrogen chloride also formed vinyl chloride when passed through a tube heated to 300° C. carrying a water-cooled tube at 80° C.[117a]

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[107] I. G. Farbenindustrie A.-G., French Patent 709,589, 1931; *Chem. Abs.*, 1932, 26, 1297; British Patents 352,474 and 352,070, 1930; *Brit. Chem. Abs.* B, 1931, 1040.

[108] Wibaut, *Rec. trav. chim.*, 1931, 50, 313; *Chem. Abs.*, 1931, 50, 313. Burkhardt and Cocker, *Rec. trav. chim.*, 1931, 50, 837; *Chem. Abs.*, 1931, 25, 4843. Wibaut and van Daltsen, *Rec. trav. chim.*, 1932, 51, 636; *Chem. Abs.*, 1932, 26, 4580.

[109] Schroeter, *Ber.*, 1898, 31, 2189; *cf.* Muthmann, *Ber.*, 1898, 31, 1880.

[110] British Patent 1,208, 1898; *J.S.C.I.*, 1899, 18, 290.

[111] Plauson, U. S. Patent 1,436,288, Nov. 21, 1922. British Patent 156,121, 1920; *Chem. Abs.*, 1921, 15, 1728.

[112] For an account of vinyl resins, see Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York, 1923.

It has also been proposed to make vinyl chloride and bromide by warming ethylene dichloride[118] or dibromide[119] respectively with alkali in methanol solution. Baxter, Edwards and Winter[119a] made vinyl chloride, together with acetylene, by heating ethylene dichloride in the presence of steam as a diluent between a temperature of 800° and 1000° C. The production of acetylene is favored by the presence of diluents, reduced pressure, or increased heating periods.

On chlorination, vinyl chloride yields 1,1,2-trichloroethane,[120] which may also be obtained directly from acetylene by interaction with a mixture of chlorine and hydrogen chloride in the presence of contact materials.[121]

Vinyl chloride may be reacted with hydrogen chloride in the presence of aluminum chloride to form ethylidene chloride (1,1-dichloroethane).[121a] When a vinyl halide, oxide or sulphide is passed over heavy metals such as iron, copper, lead, tin, bismuth, antimony, cadmium or zinc at a temperature below 400° C., 1,3-butadiene is said to result.[121b]

Staudinger, Brunner and Feisst[122] investigated the reactions of polymers of polyvinyl bromide. On reducing fractions soluble and insoluble in benzene with hydriodic acid and red phosphorus at 160° C. and then distilling with soda-lime, two impure hydrocarbons were obtained which corresponded to the formulas $C_{40}H_{82}$ and $C_{55}H_{112}$, melting at 70°-75° C. and 88°-94° C., respectively.

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[113] Chemische Fabrik Griesheim-Elektron, German Patents 278,249, 1912, 288,584, 1913, British Patent 21,134, 1913; *Chem. Abs.*, 1915, **9**, 1096; *Chem. Abs.*, 1916, **10**, 2502; *J.S.C.I.*, 1915, **34**, 818.

[114] Consortium für Elektrochem. Ind., British Patent 339,093, 1928; *Chem. Abs.*, 1931, **25**, 2438. French Patent 684,836, 1929; *Chem. Abs.*, 1930, **25**, 5307.

[115] Baxter, British Patent 349,017, 1930; assigned to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, **26**, 1945.

[116] Nieuwland, U. S. Patent 1,812,542, June 30, 1931, assigned to E. I. duPont de Nemours and Co., Inc., *Chem. Abs.*, 1931, **25**, 4894.

[117] Canadian Patent 329,042, 1933; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 1365.

[117a] Ruhrchemie A.-G., British Patents 378,873 and 378,979, 1931; *Brit. Chem. Abs.* **B**, 1932, 1071.

[118] I. G. Farbenindustrie A.-G. French Patent 694,575, 1930; *Chem. Abs.*, 1931, **25**, 1845. British Patent 349,263, 1930; *Brit. Chem. Abs.* **B**, 1931, 917.

[119] Escher Wyss Maschinenfabriken A.-G., Swiss Patent 159,148, 1933; *Chem. Abs.*, 1933, **27**, 4543.

[119a] British Patent 363,009, 1930; *Chem. Abs.*, 1933, **27**, 1365; French Patent 721,808, 1931; *Chem. Abs.*, 1932, **26**, 4067; both patents assigned to Imperial Chemical Industries, Ltd.

[120] Consortium für elektrochemische Industrie, British Patent 341,781, 1929; *Chem. Abs.*, 1931, **25**, 4893. I. G. Farbenindustrie A.-G., British Patent 349,097, 1929; *Chem. Abs.*, 1932, **26**, 5314.

[121] I. G. Farbenindustrie A.-G., British Patent 344,592, 1930; *Brit. Chem. Abs.* **B**, 1931, 621. Söll and Hennig, German Patent 547,005, 1929; assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1932, **26**, 3520.

[121a] Coleman, U. S. Patent 1,900,276, Mar. 7, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 2965.

[121b] Leyes, U. S. Patent 1,884,002, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 1015; German Patent 569.343, 1929; *Chem. Abs.*, 1933, **27**, 2163; French Patent 672,210, 1929; *Chem. Abs.*, 1930, **24**, 2142.

[122] *Helv. Chim. Acta*, 1930, **13**, 805; *Chem. Abs.*, 1931, **25**, 487.

VINYL ACETATE

The combination of acetylene with organic acids, such as acetic acid, proceeds in the presence of catalysts consisting usually of mercury salts, to yield first vinyl ester, and, if the reaction is prolonged, finally ethylidene diesters. Of the vinyl esters, the acetate is of technical importance, on account of its ease of production, the comparative cheapness of the raw materials employed in its synthesis and its ease of polymerization to light-colored resinous substances. Its production on a technical scale is described by Skirrow and Morrison[123] who maintain that the addition of acetylene to organic acids is extremely sensitive to the state and nature of the catalyst and to the temperature employed. The catalyst suggested for this process consists of a precipitate produced by the addition of sulphur trioxide (or fuming sulphuric acid) to an acetic acid solution of mercuric oxide. If acetylene is introduced into acetic acid containing this catalyst, combination occurs smoothly at 20° to 60° C. with the production of vinyl acetate, though, at higher temperatures, ethylidene diacetate becomes the major product. It is suggested that acetylene be passed at a rapid rate through the reaction mixture so that the escaping excess acetylene entrains most of the vinyl acetate (together with some acetic acid and a trace of diacetate) which is condensed. For example, 20 parts of mercuric oxide are dissolved in 2000 parts of glacial acetic acid and to this solution is added, at 85° C., 276 parts of a precipitate formed by reacting 34 parts of sulphur trioxide with 242 parts of glacial acetic acid at 20° C. The mixture is brought to about 25° C. and a great excess of acetylene gas is passed through, the temperature being allowed to rise to 35° C. with an average temperature of about 34° C. The gas and entrained vapors are cooled and the condensate obtained is fractionated to yield vinyl acetate. At the end of 10 to 12 hours, the rate of acetylene absorption diminishes owing to reduction of the catalyst, and at this time the yield of vinyl acetate is about 70 per cent based on the acetic acid combined and 78 per cent based on the acetylene consumed. The amount is said to be 115 parts of vinyl acetate per part of mercuric oxide used.

A modification of the above process in which acetylene is led into acetic acid at 5°-25° C. in the presence of a mercury compound, sulphacetic acid, and acetic anhydride, to yield vinyl acetate has been suggested.[124] Dykstra and Sly[125] produced vinyl esters by passage of acetylene into a hot mixture of an organic acid and an aliphatic hydrocarbon distillate. According to Herrmann, Deutsch and Baum[126] vinyl esters may be produced by vapor-phase combination of acetylene and an organic acid in the presence of a heated catalyst, such as zinc acetate or activated carbon, the reacting gases having a vapor velocity of 350 liters per hour per liter of reaction space. Acetylene and acetic acid also combine to form vinyl acetate and ethylidene diacetate when passed through a tube heated to 200° C. containing a water-cooled tube at 20° C.[126a]

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[123] British Patents 308,169 and 308,170, 1928; *Chem. Abs.*, 1930, 24, 129; Canadian Patent 318,838, 1932; *Chem. Abs.*, 1932, 26, 1944; German Patent 559,436, 1929; *Chem. Abs.*, 1933, 27, 736; all patents assigned to Canadian Electro Products Co., Ltd.

[124] Imperial Chem. Industries, Ltd., British Patent 351,318, 1930; *Chem. Zentr.*, 1931, 2, 1754.

[125] Dykstra and Sly, U. S. Patent 1,786,647, Dec. 30, 1931; Dykstra, U. S. Patent 1,849,616, Mar. 15, 1932; *Chem. Abs.*, 1932, 26, 2752; both patents assigned to E. I. duPont de Nemours & Co., Inc.

[126] U. S. Patent 1,822,525, Sept. 8, 1931; *Chem. Abs.*, 1931, 25, 5900; assigned to Consortium für Elektrochemische Industrie.

[126a] Ruhrchemie A.-G., British Patents 378,873 and 378,979, 1931; *Brit. Chem. Abs.* B, 1932, 1071.

Vinyl esters may be smoothly halogenated at 0° C. to yield 1,2-dihalogen esters. Chlorination of vinyl acetate results in the production of 1,2-dichloroethyl acetate.[127] Acid anhydrides result on reacting vinyl esters with carboxylic acids. For example, vinyl acetate and acetic acid[127a] react in the presence of catalysts such as sulphuric, phosphoric, benzenesulphonic, sulphoacetic acid and sulphur chloride to form acetic anhydride and ethylidene diacetate.

VINYL ETHERS

Divinyl ether, $CH_2{=}CHOCH{=}CH_2$, a very interesting unsaturated ether partly polymerizable by benzoyl peroxide, is a liquid of boiling point 28.3° ± 0.2° C. at 760 mm. It has been prepared in a pure state by Ruigh and Major[128] by heating $\beta\beta'$-dichlorodiethyl ether with potash at 200° to 240° C. Aromatic vinyl ethers may be prepared either from vinyl halides[129] or ethylene dihalides by interaction with phenols in alkaline media. Thus an 80 per cent yield of vinyl phenyl ether, boiling point 155°-156° C., is obtained by heating ethylene dichloride with caustic soda, phenol, and alcohol in an autoclave at 180° to 200° C.[130] Vinyl and other unsaturated ethers may also be produced by passing the vapor of an aliphatic or aromatic acetal over a catalyst.[130a] The catalyst may consist of silver, gold, platinum or palladium mixed with metals of groups I to IV and VI to VIII of the periodic system or their oxides, phosphates or silicates. Alkyl vinyl ethers have also been prepared by Chalmers[130b] by heating alkyl 2-bromoethyl ethers with sodium hydroxide.

ETHYLIDENE ESTERS

As previously stated, the ethylidene diesters of the general formula CH_3CHX_2, where X represents an acidic group, are the ultimate products of the reaction between acetylene and organic acids. Of these diesters, ethylidene diacetate, $CH_3CH(OOCCH_3)_2$, a liquid of boiling point 170° C., is by far the most important. Technical interest in this ester is almost entirely centered around its ready decomposition under the influence of heat, which results in the formation of acetic anhydride, together with acetaldehyde, a reaction which has been known for many years. According to one method, acetic anhydride is conveniently made from this ester by rapidly heating it to 300° to 450° C.[131]

The methods of producing ethylidene diacetate usually involve the introduction of acetylene into warm acetic acid containing a mercury catalyst.[132] The same catalysts are used as for making vinyl esters. The essential difference in the processes for making the two types of compounds is that ethylidene diesters require a higher temperature. A process of Skirrow and Morrison[133] involves the passage of acetylene into acetic acid, maintained at about 80° C., and containing a catalyst of a mercuric salt of sulphacetic acid. For example, 10 parts of mercuric oxide are dissolved in 2000 parts of glacial acetic acid and to this is added, at 85° C., 276 parts of a precipitate formed by reacting 30 parts of sulphur trioxide with 246 parts of glacial acetic acid at about 20° C. After precipitation of the catalyst, the mixture is brought to a temperature of 60° to 70° C. and an excess of acetylene is passed through, the temperature being allowed to rise to 80° C. The main product is ethylidene diacetate, which, together with a little vinyl acetate and some free acid, is carried over by the escaping excess of acetylene. After 1 to 3 hours, depending upon the scale of operations and the cooling capacity, the rate of acetylene absorption diminishes owing to the large percentage conversion of the acid and to the reduction of the catalyst.

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[127] Ellis, British Patent 325,115, 1929; assigned to Soc. des usines chimiques Rhône-Poulenc; *Brit. Chem. Abs.* **B**, 1930, 409.

[127a] Deutsch and Herrmann, German Patent 503,131, 1927; *Chem. Abs.*, 1930, **24**, 5045; German Patent 526,795, 1928; *Chem. Abs.*, 1931, **25**, 4559; German Patent 537,363, 1928; *Chem. Abs.*, 1932, **26**, 999; British Patent 288,549, 1927; *Chem. Abs.*, 1929, **23**, 608; all patents assigned to Consortium für elektrochemische Industrie G.m.b.H.

[128] *J.A.C.S.*, 1931, **53**, 2662; also Hibbert, Canadian Patent 311,819, 1931.

[129] I. G. Farbenindustrie A.-G., German Patent 513,679, 1927; *Chem. Abs.*, 1931, **25**, 1841.

[130] Ernst and Berndt, German Patent 525,188, 1929; *Chem. Abs.*, 1931, **25**, 4284; Reppe, German Patent 559,523, 1930; *Chem. Abs.*, 1933, **26**, 736; British Patent 341,074, 1929; *Chem. Abs.*, 1931, **25**, 4891; French Patent 38,910, 1930; *Chem. Abs.*, 1932, **26**, 1616; all patents assigned to I. G. Farbenindustrie A.-G.

[130a] I. G. Farbenindustrie A.-G., British Patent 345,253, 1929; *Chem. Abs.*, 1932, **26**, 156.

[130b] Canadian *J. Res.*, 1932, **7**, 464; *Brit. Chem. Abs.* **A**, 1933, 144.

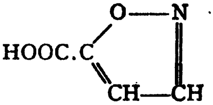
[131] Matheson, U. S. Patent 1,872,479, Aug. 16, 1932; *Chem. Abs.*, 1932, **26**, 5971; British Patent 368,835, 1930; *Brit. Chem. Abs.* **B**, 1932, 670; both patents assigned to Canadian Electro Products Co.; *cf.* Walter, German Patent 495,334, 1928, to Verein für chemische Industrie A.-G.; *Chem. Abs.*, 1930, **24**, 3251.

[132] Klatte, U. S. Patent 1,084,581, Jan. 13, 1914; *J.S.C.I.*, 1914, **33**, 219; British Patent 14,246, 1913; *J.S.C.I.*, 1914, **33**, 767; both patents assigned to Chem. Fabrik Griesheim-Elektron. Boiteau, British Patent 15,919, 1914; *Chem. Abs.*, 1916, **10**, 93; Soc. des usines du Rhône anciennement Gilliard, P. Monnet et Cartier, British Patents 112,765 and 112,766, 1917; *Chem. Abs.*, 1918, **12**, 1050. Walter, German Patent 556,775, 1927; *Chem. Abs.*, 1933, **27**, 312; German Patent 571,318, 1928; *Chem. Abs.*, 1933, **27**, 2696; both patents assigned to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler.

A method of purification of crude ethylidene diacetate by agitation with an aqueous salt solution of density greater than that of the ester, followed by stratification and separation, has been developed.[134]

MISCELLANEOUS REACTIONS OF ACETYLENE

When passed slowly into fuming *nitric acid,* acetylene combines to form a solid acid of the formula, $C_4H_3O_3N$, melting at 149° C., which was described by Baschieri[134a] and Testoni and Mascarelli.[134b] It was later subjected to a careful examination by Quilico and Freri,[135] who concluded, from its properties and chemical reactions, that the substance was an isoxazole-*a*-carboxylic acid of the formula,



With *hypochlorous acid,* acetylene combines to yield dichloroacetaldehyde,[136] or $CHCl_2CHO$.

Acetylene may be condensed with *ammonia* or *amines* at elevated temperatures in the presence of catalysts to yield a number of compounds, among which nitriles and pyridine bases may be specially mentioned. The preparation of acetonitrile by condensing acetylene with ammonia has been the subject of a number of investigations.[137] Acetylene can be converted into pyridine bases without the formation of acetonitrile by passing a mixture of ammonia and acetylene, over a heated catalyst of zinc sulphate, zinc chloride, cadmium chloride or other inorganic salt capable of combining with ammonia.[138] Acetonitrile and other nitriles[139] may be produced without simultaneous formation of pyridine bases, by condensing acetylene with ammonia or amines at high temperatures in the presence of compounds of metals of groups II to VII of the periodic system, not reducible under the working conditions, and employing a gas velocity not exceeding 50 liters of acetylene per hour per liter of catalyst. Good catalysts are mixtures of metallic oxides not reducible at 450° C. or single non-reducible compounds of zinc, aluminum, zirconium, thorium, tin, vanadium, bismuth, molybdenum and tungsten, supported on silica or alumina gel. The nitriles yield acetic acid on saponification, ammonium salts being obtained as by-products.[139a] When saponified with alcohols at 50° to 250° C. in the vapor phase, esters are formed.[139b] Rötger[140] prepared products containing 80 per cent pyridine bases consisting predominantly of picolines, which can be used for the protection of plants, by passing ammonia and acetylene over silica gel and finely divided cadmium at 320° C. Another process[141] consists in condensing acetylene with ammonia or amines together with steam in the presence of condensing catalysts at 250° to 500° C. and followed by mixing the reaction products with hydrogen and passing them over a hydrogenating catalyst at 180° to 250° C. Thus, a mixture of acetylene, ammonia, and hydrogen is passed at 350° C. over a catalyst of zinc oxide and thorium oxide on silica gel and then at 150° C. over finely divided nickel on silica gel to yield piperidine and monoethylamine. The treatment of aniline, acetylene, and hydrogen to furnish tetrahydroquinoline, and also of acetylene, hydrogen, methane and ammonia to obtain ethylamine and acetonitrile, has been suggested by Nicodemus.[142]

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[133] British Patent 335,223, 1930; to Canadian Electro Products Co.; *Chem. Abs.*, 1931, **25**, 1261.

[134] Brown, British Patent 353,318, 1930; assigned to Courtaulds, Ltd.; *Brit. Chem. Abs.* **B**, 1931, 1086.

[134a] *Atti. real. accad. Lincei,* 1900, (5) **9** (1), 391; *Chem. Soc. Abs.,* 1900, **78** (1), 534; *Gazz. chim. ital.*, 1901, **31** (2), 462.

[134b] *Atti. real. accad. Lincei,* 1901, (5) **10** (1), 442; *Chem. Soc. Abs.,* 1901, **80** (1), 494; *Gazz. chim. ital.*, 1902, **32** (1), 202; Mascarelli, *Gazz. chim. ital.,* 1903, **33** (2), 319; *Chem. Soc. Abs.*, 1904, **86** (1), 277.

[135] *Gazz. chim. ital.,* 1929, **59**, 930; *Chem. Abs.,* 1930, **24**, 3484.

[136] Wittorf, *Chem. Zentr.,* 1900, **2**, 29.

[137] See, for example, Stuer and Grob, British Patent 109,983, 1916; assigned to Chem. Fabrik Rhenania; *J.S.C.I.*, 1917, **36**, 1194; Ruhrchemie A.-G.; British Patents 378,873 and 378,979, 1931; *Brit. Chem. Abs.* **B**, 1932, 1071.

[138] Nicodemus, U. S. Patent 1,882,518, Oct. 11, 1933; *Chem. Abs.*, 1933, **27**, 736; German Patent 479,351, 1927; *Chem. Abs.,* 1929, **23**, 4709; British Patent 283,163, 1928; *Brit. Chem. Abs.* **B**,

Vinyl cyanide is formed when acetylene and hydrogen cyanide are led over a catalyst consisting of, for example, a mixture of barium cyanide and active carbon, according to Baum and Herrmann.[142a]

Thiophene and similar sulphur-containing compounds are made by the reaction of acetylene with sulphur, metallic sulphides or hydrogen sulphide. They may be produced, for example, by conducting acetylene over pyrites heated to 280°-310° C.[143] The catalytic combination of acetylene and hydrogen sulphide in the vapor phase to yield thiophene has been described. A mixture of acetylene and hydrogen sulphide and a heated catalyst of nickel hydroxide mixed with a silicate cement or partially reduced bauxite is used.[144]

The manufacture from acetylene of liquid condensation products containing

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1929, *275*; all patents assigned to I. G. Farbenindustrie A.-G. The product formed by condensation of ammonia and acetylene can be separated by washing out the gases (ammonia and acetylene) leaving the reaction chamber with the liquid products formed, according to Ernst and Nicodemus (U. S. Patent 1,872,432, Aug. 16, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 6081).

[139] Rötger, German Patent 526,798, 1929; *Chem. Abs.*, 1931, **25**, 4556; German Patent 528,897, 1929; *Chem. Abs.*, 1931, **25**, 4891; British Patent 295,276, 1928; *Brit. Chem. Abs.* **B**, 1930, 50; all patents assigned to I. G. Farbenindustrie A.-G.

[139a] Rötger, German Patent 560,543, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 1007.

[139b] I. G. Farbenindustrie A.-G., British Patent 366,106, 1930; *Chem. Abs.*, 1933, **27**, 1891.

[140] German Patent 541,655, 1928; *Chem. Abs.*, 1932, **26**, 2548; British Patent 321,177, 1929; *Chem. Abs.*, 1930, **24**, 2757; both patents assigned to I. G. Farbenindustrie A. G. See also Schlecht and Rötger, U. S. Patent 1,894,792, Jan. 17, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2454.

[141] I. G. Farbenindustrie A.-G., British Patent 334,193, 1929; *Brit. Chem. Abs.* **B**, 1930, 1103.

[142] German Patent 479,351, 1927; *Chem. Abs.*, 1929, **23**, 4709; German Patent 504.238, 1927; *Chem. Abs.*, 1930, **24**, 5305; German Patent 516,765, 1928; *Chem. Abs.*, 1931, **25**, 1839; German Patent 547,518, 1929; *Chem. Abs.*, 1932, **26**, 3513; all patents assigned to I. G. Farbenindustrie A.-G. See also British Patent 283,163, 1927; *Chem. Abs.*, 1928, **22**, 3892.

[142a] German Patent 559,734, 1930; assigned to Consortium für elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1933, **27**, 735.

[143] Steinkopf and Kirchhoff, British Patent 16,810, 1912; *Chem. Abs.*, 1914, **8**, 416; *Ann.*, 1914, **403**, 1; *Chem. Abs.*, 1914, **8**, 1416.

[144] Stuer and Grob, British Patent 109,983, 1916; assigned to Chemische Fabrik Rhenania; *Chem. Abs.*, 1918, **12**, 370.

both nitrogen and sulphur has been accomplished.[145] Such materials so obtained may be employed as denaturants for alcohols and as flotation agents. The liquid condensation products are made by passing a mixture of acetylene and ammonia over iron pyrites at 350° to 450° C. and consist of mixtures of nitriles, pyridine and other nitrogen bases and organic sulphur compounds such as ethyl mercaptan, thiophene as well as mustard oils containing the characteristic grouping –NCS. For example, a mixture of equal parts of acetylene, ammonia, and steam is passed over granular pyrites at 350° C. The condensate consists of two layers: an aqueous layer containing acetonitrile, water-soluble pyridine bases, sulphur compounds, and ammonia; and an oily layer, made up of about 20 per cent of thiophene, up to 30 per cent of pyridine bases, besides nitriles, mercaptans, and high-boiling sulphur compounds of unknown nature. A fraction, boiling below 200° C., of the oily layer may be used as a denaturant for ethyl alcohol, the amount required being about 5 cc. per liter of alcohol.

Bergmann and Bondi[146] studied the action of phosphorus pentachloride on acetylene derivatives. Phenylacetylene, on treatment with phosphorus pentachloride and subsequent hydrolysis, is converted to β-chloro-β-phenylvinylphosphinic acid, which may be changed by potassium hydroxide into phenylacetylenylphosphinic acid.

On treatment with potassium mercuri-iodide or with mercuric acetate, vinylacetylene yields divinylethynyl-mercury, a crystalline solid melting at 144° to 145° C. Reactions of the compounds formed on treating vinylacetylenes with mercury salts have been studied by Carothers, Jacobson and Berchet.[147]

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[145] Müller, Schlecht and Rötger, German Patent 512,712, 1927; *Chem. Abs.*, 1931, **25**, 1328; British Patent 326,795, 1928; *Brit. Chem. Abs.* **B**, 1930, 548; *cf.* Schlecht and Rötger, German Patent 513,410, 1928; *Chem. Abs.*, 1931, **25**, 1329; all patents assigned to I. G. Farbenindustrie A.-G.

[146] *Ber.*, 1933, **66**, 278; *Chem. Abs.*, 1933, **27**, 2431; *Brit. Chem. Abs.* **A**, 1933, 290.

[147] *J.A.C.S.*, 1933, **55**, 4665.

Chapter 29

Halogenation of Methane. Properties and Uses of Halogen Derivatives

The behavior of saturated hydrocarbons, i.e., paraffins and cycloparaffins, toward halogens is fundamentally different from that of unsaturated hydrocarbons. Whereas halogens combine additively with unsaturated hydrocarbons to form more saturated derivatives, they substitute or replace hydrogen of saturated hydrocarbons. The hydrogen atoms thus displaced are eliminated as hydrogen halide. The progressive substitution of hydrogen atoms of completely saturated hydrocarbons by chlorine may be expressed by the following general series of reactions:

$$C_nH_{2n+2} + Cl_2 \longrightarrow C_nH_{2n+1}Cl + HCl,$$
$$C_nH_{2n+1}Cl + Cl_2 \longrightarrow C_nH_{2n}Cl_2 + HCl; \text{ etc.}$$

The order of decreasing reactivity of halogens with paraffin hydrocarbons is fluorine, chlorine, bromine and iodine, i.e., the higher the molecular weight the smaller the tendency to substitute a hydrogen atom of the hydrocarbon. Fluorine often reacts with explosive violence but iodine does not appear to react at all. On account of the comparative cheapness of chlorine, the chlorination of hydrocarbons has been much more extensively studied than the action of the other halogen elements. Many of the chlorohydrocarbons formed from the paraffins are of industrial value as solvents, while the monochlorinated products, the alkyl chlorides, have received much attention because of their use in the manufacture of alcohols.

The Chlorination of Methane

Both the abundance of methane and the comparative cheapness of chlorine favor the commercial application of the chlorination of methane for the production of one or other of the chloro-derivatives. The extensive amount of work on this subject indicates the great interest in this problem. The products of the chlorination usually consist of all of the four possible chlorination products and in general it is not possible to control the reaction so as to produce one substance only.

Because of the very highly exothermic nature of the chlorination reactions, the successful control of the process is often a matter of difficulty even on a laboratory scale. Furthermore, there is always a danger of chlorination proceeding extremely violently and even with explosive force. When this occurs high reaction temperatures are attained and the main products are carbon and hydrogen chloride, formed according to the reaction:

$$CH_4 + 2Cl_2 \longrightarrow C + 4HCl.$$

High temperature chlorination of methane and other hydrocarbons can, in fact, be utilized for the production of lampblack or carbon black together with hydrogen chloride.[1]

The actual heats of reaction of the various chlorination processes cannot be calculated with certainty, owing to the unreliability of the thermal data, but the approximate figures for the gaseous reactions at 400° C. are as follows:[2]

$$\begin{aligned}
CH_4 + Cl_2 &\longrightarrow CH_3Cl + HCl + 33\text{ Cal.}\\
CH_4 + 2Cl_2 &\longrightarrow CH_2Cl_2 + 2HCl + 60\text{ Cal.}\\
CH_4 + 3Cl_2 &\longrightarrow CHCl_3 + 3HCl + 94\text{ Cal.}\\
CH_4 + 4Cl_2 &\longrightarrow CCl_4 + 4HCl + 137\text{ Cal.}
\end{aligned}$$

Although there is no rigorous parallelism between the heats of reaction and reaction velocity, nevertheless as there is a slight increase in the heat of reaction with progressive chlorination, it may be expected that the chlorination reaction will tend to go to completion, i.e., to produce carbon tetrachloride, unless some temperature control is maintained. In fact Jones, Allison and Meighan[2] in their work on the chlorination of natural gas stated:

> "If the temperature of the reaction chamber rises above 500° C., the reaction proceeds according to the formulas: $CH_4 + 2Cl_2 = C + 4HCl$, and $C_2H_6 + 3Cl_2 = 2C + 6HCl$. This reaction is explosive in character and gives no hydrocarbon chlorides. The heat control of the reaction is the important phase of the problem that must be solved before the work can be placed upon a plant basis."

Furthermore, active catalysts will evidently favor the formation of polychlorinated derivatives. Also thermodynamic calculations indicate the chlorination reaction possesses a great tendency to proceed even at comparatively low temperatures. These deductions are in accord with the observed facts.

The methods which have been used for effecting the chlorination of methane have been of diverse character. In general, chlorination has been brought about by exposing a mixture of methane and chlorine to the action of actinic light, heat, catalysts, and other activating influences such as the silent electric discharge. The greatest difficulties arise in controlling the process to avoid both explosion and the formation of all but the desired chlorinated product. Proper control of concentrations, temperature, and activating influence minimizes, though it does not entirely overcome, the latter difficulty while danger of explosion may be obviated to some extent by dilution of the hydrocarbon with inert gases, such as carbon dioxide, nitrogen, steam, hydrogen chloride, or chlorinated substances and also by accurate regulation of the quantities of chlorine admitted to reaction. Chlorination in inert liquid diluents has been utilized.[3]

Chlorination of methane may also be effected by means of certain reagents which give rise to chlorine in the reaction mixture, such as, for example, sulphuryl chloride, phosgene or antimony pentachloride, while hydrogen chloride has been proposed as a source of nascent chlorine.

It is convenient to subdivide the work on the chlorination of methane into the following main headings, namely, (1) thermal, (2) catalytic, (3) photochemical, and (4) other modes of chlorination.

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[1] Mott, U. S. Patent 1,259,121, March 12, 1918; *J.S.C.I.*, 1918, **37**, 313A; Rumbarger, U. S. Patent 1,401,738, Dec. 27, 1922; *Chem. Abs.*, 1922, **16**, 995. See also Chapter 7.

[2] Jones, Allison and Meighan, *U. S. Bureau Mines, Tech. Paper* 225, 1921.

[3] Reviews of the chemistry of the chlorination of methane have been published by Wegscheider (*Z. Elektrochem.*, 1922, **28**, 99) and by Egloff, Schaad and Lowry (*Chem. Reviews*, 1931, **8**, 1).

THERMAL CHLORINATION

Like all other chemical processes, chlorination of methane is greatly accelerated by heat alone and may become exceedingly violent if suitable precautions are not taken to moderate the reaction. According to Jones, Allison and Meighan,[4] the reaction in the dark between chlorine and natural gas begins at a temperature slightly below 250° C. and at this lower temperature the chlorine reacts with the ethane present in such gas in preference to the methane. At 250° C. the chlorination was only partial, but at 300° C., and higher, the maximum amount of chlorine was used and the reaction took place smoothly without carbon deposition. In the presence of light, however, and particularly of light from the electric arc, chlorination takes place very readily at much lower temperatures and, within certain concentrations of reactants, may become explosive.

Pease and Walz[5] measured the rate of thermal chlorination of methane in the neighborhood of 250° C. using a cylindrical catalyst tube of Pyrex glass. At this temperature it was found quite safe to work with mixtures containing an excess of chlorine and which are subject to explosion at higher temperatures. Under the conditions employed by Pease and Walz the only reactions occurring were straightforward chlorinations to methyl chloride, methylene dichloride, chloroform, and carbon tetrachloride. With excess of methane ($3CH_4 : 1Cl_2$) and small conversion of chlorine (e.g., 25 per cent), methyl chloride is the main product of the thermal chlorination. The observation was made that the reaction under these conditions is powerfully inhibited by traces of oxygen, which suggests that a chain mechanism is involved.

The chlorination of methane, and also of other paraffin hydrocarbons, is undoubtedly a stepwise reaction in which the mono-chloro-compound first produced is progressively chlorinated to higher chlorinated products. The thermodynamic tendency appears to be toward complete chlorination over a wide temperature range. The stepwise nature of the chlorination process of methane is amply proved by the work of a large number of observers, particularly of Bedford.[6] Furthermore, methyl chloride may be readily chlorinated either to methylene dichloride, chloroform, or carbon tetrachloride or to a mixture of these substances by thermal chlorination in the presence or absence of catalysts.[7] In connection with the mechanism of the methane chlorination, Martin and Fuchs[8] have calculated the following equation:

$$y_m = \frac{\lfloor\underline{n}}{\lfloor\underline{m}\;\lfloor\underline{n-m}}\,(100-x)\left[\left(\frac{100}{100-x}\right)^{\frac{1}{n}}-1\right]^m$$

The theoretical and practical results are, however, only in agreement in certain cases. This general formula gives the percentage of initial substance (e.g., methane), represented by y_m, converted into the m^{th} product of a reaction of n bimolecular stages, in terms of the total percentage of initial substance consumed (x). For example, in the chlorination of methane, the percentage of methane converted to dichloromethane is obtained by substituting 4 for n, 2 for m, and the total percentage of methane consumed in the entire chlorination for x in the equation.[8a]

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[4] *U. S. Bur. Mines Tech. Paper*, **255**, 1921.

[5] *J.A.C.S.*, 1931, **53**, 382; *ibid.*, 1931, **53**, 3728.

[6] *J. Ind. Eng. Chem.*, 1916, **8**, 1090.

[7] Damoiseau, *Compt. rend.*, 1880, 91, 1011; Mason and Wheeler, *J.C.S.*, 1931, 2282; I. G. Farbenindustrie A.-G., British Patent 283,119, 1928; French Patent 646,661, 1927; Carter and Coxe, U. S. Patent 1,572,513, Feb. 9, 1926; assigned to S. Karpen and Bros.

[8] *Z. Elektrochem.*, 1921, **27**, 150.

The purely thermal chlorination of methane at very high temperatures has been examined experimentally by Mason and Wheeler.[9] The use of very high space velocities (as high as 30,000 reciprocal minutes at 1400° C.) in conjunction with high temperatures results in a cutting short of the chlorination process and consequently in a relatively large production of methyl chloride in preference to higher chlorinated products. Thus for example by passing a mixture of 1 volume of chlorine and 7 volumes of methane through an alumina-silica refractory reaction tube heated to 1200° C. and at a space velocity of 23,800 reciprocal minutes, the yields of products calculated on the chlorine input were: methyl chloride 39.2 per cent, methylene dichloride 13.4 per cent, chloroform 20 per cent, and carbon tetrachloride 2.0 per cent. In later experiments somewhat lower temperatures (800° to 900° C.) and lower space velocities were used and it was found advantageous to pack the reaction tube with refractory material. Passage of a mixture of 9.2 volumes of methane and 1.0 volume of chlorine at a space velocity of 9000 reciprocal minutes through the packed refractory tube at 900° C. resulted in the formation of the following yields of products (calculated on the chlorine input): methyl chloride 36.3 per cent, methylene dichloride 6.46 per cent, and chloroform 2.35 per cent, with practically no carbon tetrachloride. It is evident, therefore, that this method of chlorination, consisting essentially in the use of high temperatures in conjunction with high space velocities (i.e., short heating periods) is very efficient for the production of methyl chloride with the coincident production of only small amounts of higher chlorinated products. It is very interesting to note that the results of Mason and Wheeler for the high temperature chlorination of both methane and methyl chloride were in quite good agreement with the theoretical predictions of Martin and Fuchs. Some of the experimental results of Mason and Wheeler are given in Table 117:

TABLE 117.—*High Temperature Chlorination of Methane* (*Mason and Wheeler*).

Experiment	1	2	3	4	5	6
Temperature ° C.	900	900	900	900	900	900
Space velocity (min.^{-1})	9400	9400	9300	5700	5600	8100
Ratios $Cl_2:CH_4$	1:2.97	1:4.85	1:8.8	1:8.6	1:8.4	1:7.5
Yield of CH_3Cl (% on chlorine input)	48.3	50	42.5	82.1	70.5	75.6
Chlorine balance (% on input)						
CH_3Cl	24.1	25.0	21.3	41.1	35.2	37.8
CH_2Cl_2	14.2	9.9	4.5	9.7	8.4	5.6
$CHCl_3$	1.43	—	4.4	—	5.0	3.7
CCl_4	—	—	—	—	—	—
Total in washers ($Cl_2 + HCl$)	54.7	52.3	51.1	51.5	51.3	51.8
Total chlorine balance	94.5	87.1	81.2	102.3	99.9	98.8
Yield of CH_3Cl calculated on 100% Cl_2 balance	59.3	75.8	80.2	—	—	77.8

CHLORINATION WITH CATALYSTS

In general, catalysts tend to accelerate the chlorination of methane and appear to favor the formation of higher chlorinated products than methyl chloride.

[8a] In the above equation $\underline{|n}$ represents factorial n, i.e., when $n = 4$, $\underline{|4}$ is $4 \times 3 \times 2 \times 1$. It is to be understood that $\underline{|0}$ is taken to be unity. The number of bimolecular stages (n) is the number of replaceable hydrogens in the molecule.

[9] *J.C.S.*, 1931, 2282.

A variety of catalysts has been used and these include metallic chlorides (such as ferric chloride, silver chloride, partially reduced cupric chloride, aluminum chloride, manganous chloride, antimony pentachloride, molybdenum pentachloride, coke impregnated with the chlorides of platinum, zinc, cadmium, tin, and lead) as well as various adsorbent materials, such as activated charcoal, and animal charcoal admixed with finely divided calcium oxide. These catalysts have been used in conjunction with temperatures up to 300° C. and above, and since chlorination can proceed at these temperatures without the aid of catalysts, the results obtained cannot always be solely attributed to the effect of these catalysts.

The effect of various solid materials in promoting the combination of chlorine and methane was investigated by Phillips,[10] who passed a mixture of chlorine and natural gas through heated tubes packed with sand, asbestos, and bone black. He found that the tendency was to form methyl chloride and carbon tetrachloride with very little of the intermediate products. When the temperature became too high, carbon was deposited.

The chlorination of natural gas in the presence of pumice, alone and impregnated with cupric and managanous chlorides, was examined by Tolloczko and Kling.[11] In order to eliminate the possibility of an explosion, which was very prone to occur in sunlight and also at higher temperatures, chlorination was carried out with an excess of one of the reactants and at as low a temperature as possible. Using pumice as a catalyst at 400° C. and an excess of chlorine, the products of the chlorination consisted mainly of carbon tetrachloride together with various chloro-hydrocarbons derived from ethane. Poor yields were obtained when an excess of the hydrocarbon gas was employed. A catalyst of pumice impregnated with cupric chloride was more efficacious than a pumice catalyst soaked with manganous chloride, and could be used at a lower temperature. Passage of a mixture of chlorine and natural gas over the former catalyst at 300° C. led to the production of methyl chloride, methylene dichloride and a little ethyl chloride as well as of chloroform, carbon tetrachloride, tetrachloroethylene, acetylene tetrachloride, and, in the fraction boiling above 165° C., dichloroethane.

An experimental investigation of the chlorination of nearly pure methane (containing only small amounts of oxygen and nitrogen and no olefins) in the presence of antimony pentachloride and ferric chloride at 360° to 400° C. has been reported by Pfeifer, Mauthner and Reitlinger.[12] The dried hydrocarbon was mixed with chlorine and passed through a heated quartz reaction tube containing the catalyst, while the gaseous products of the reaction were passed through two spiral condensers, the first of which was water-cooled and the second maintained at —35° to —45° C. by means of alcohol and solid carbon dioxide. The distillate in the first receiver contained dichloromethane, chloroform, and carbon tetrachloride, while that in the second receiver was mostly methyl chloride. The best results were obtained by using ferric chloride as a catalyst. With this catalyst and using a methane-chlorine volume ratio of 2:1, 85 per cent of the chlorine was converted and the product consisted of 30 per cent of methyl chloride (calculated on chlorine) as well as about equal amounts of dichloromethane and chloroform. Increasing the methane-chlorine ratio to 3:1 resulted in an increase in the methyl chloride yield to 40 per cent of the theoretical, based on the chlorine consumption. Attempts made to increase the yield of carbon tetrachloride by increasing the chlorine content of the reacting gases resulted in violent explosions. However, by employing an inert diluent, namely nitrogen, in conjunction with higher chlorine-methane ratios, risks of explosion were minimized and the products then consisted only of chloroform and carbon tetrachloride. Thus passage of a mixture of 1 volume of methane, 2 volumes of nitrogen and 3 volumes of chlorine over the catalyst resulted in the formation of the two higher chlorinated products only. Table 118 shows some of the experimental results of these workers.

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[10] *Amer. Chem. J.*, 1894, 16, 361.

[11] *Abhandl. Krakauer. Akad. Wissensch.*, 1912, 52, 295; *Chem. Zentr.*, 1913, 2, 98; *J.S.C.I.*, 1913, 32, 742A.

[12] *J. pr. Chem.*, 1919, 99, 239; *J.S.C.I.*, 1919, 38, 924A.

TABLE 118.—*Catalytic Chlorination of Methane (Pfeifer, Mauthner, and Reitlinger).*

Catalyst	Volume Ratio $CH_4:Cl_2$	Chlorine Reacting Per Cent	Products: Per Cent on Total Chlorine Used			
			CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
$SbCl_5$	1:2	64	0	5.8	20.3	5.9
$FeCl_3$	1:2	83.6	trace	13.25	22.2	6.35
$FeCl_3$	1:1	86.4	5.8	15.7	21.7	0

Important work on the chlorination of a Pittsburgh natural gas (containing 89.5 per cent CH_4, 10.1 per cent C_2H_6, and 0.4 per cent N_2) in the presence of various catalysts was carried out by Jones, Allison and Meighan.[13] The best catalysts tried were adsorbent charcoal (made from coconut shells), an active carbon called "Batchite", made from anthracite, and metallurgical coke, both alone and impregnated with the nitrates or chlorides of nickel, zinc, cadmium, barium, platinum, copper, etc., or with mixtures of these nitrates and chlorides. Such substances as silica gel, porcelain, asbestos, glass wool and pumice were also tried but proved to be very poor catalyzers. The chlorination process proceeded satisfactorily in the presence of the better catalysts at temperatures above 300° C., the optimum temperature being about 400° C. Temperatures above 500° C. were undesirable owing to the violence of the reaction and the deterioration of the catalysts under such conditions. The products of the chlorination consisted not only of all the four chloromethanes but also of the higher chlorinated ethanes, notably hexachloroethane. The salient features of this important investigation may be summarized as follows:

(1) Natural gas may be completely chlorinated to carbon tetrachloride in one operation with yields of over 90 per cent of the chlorinated products on using chlorine-methane ratios of 5:1 to 2.5:1.

(2) For the production of chloroform, coke impregnated with metals such as platinum, nickel, and iron are most suitable. Using platinized coke, 50 per cent of gas was converted into chloroform.

(3) Activated charcoals and "Batchite" furnished the highest yields of carbon tetrachloride.

(4) The highest yield (31 per cent) of methyl chloride was obtained by using a ratio of 2 volumes of chlorine to 1 volume of natural gas in the presence of coke impregnated with nickel, tin, and lead.

(5) Addition of small amounts (up to 1 per cent) of moisture to the reacting gases was stated to aid chlorination.

(6) Ethane tends to chlorinate much more readily than methane.

The catalysts which showed a high adsorption capacity for chlorine were unsuitable for the production of methyl chloride and favored the production of higher chlorinated products, especially carbon tetrachloride.[14] In view of the obviously cumulative nature of the process and the thermodynamic tendency for complete chlorination to occur, it is to be expected that active catalysts will not favor the formation of methyl chloride but rather of carbon tetrachloride.

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[13] Jones and Allison, *J. Ind. Eng. Chem.*, 1919, 11, 639; Jones, Allison and Meighan, *U. S. Bur. Mines Tech. Paper* 225, 1921.

[14] It is also possible that such catalysts possess a powerful tendency to absorb the chlorides of methane rather than methane itself and hence hold them in the reaction zone until chlorination was complete.

Schleede and Luckow[15] made a study of the chlorination of methane at temperatures of the order of 400° C. in quartz and glass reaction tubes with and without the addition of catalysts. When the reacting gases were used in molar proportions, inflammation occurred but the flame was not permanent except when an excess of chlorine was used. Ignition was not observed when methane was present in excess but in this case the chlorine was only quantitatively utilized if the temperature was above a certain minimum depending upon the precise composition of the reacting gas mixture and upon the rate of flow. These phenomena were not greatly affected by the presence of catalysts or by an increase in temperature of 100° C. above the minimum. The rate of flow of the reacting gases over the surface of the catalyst was found to exert a marked influence on the nature of the products. If comparatively low rates of flow were employed, no ignition occurred but an increased production of chloroform and carbon tetrachloride took place at the expense of methyl chloride and dichloromethane. However, when the velocity of the reacting gases per unit of surface exceeded a certain value, the reaction was found to tend more and more to a steady ignition and increased formation of higher products (chlorinated products of higher paraffins) took place principally at the expense of the chloroform. Even at rates of flow below the ignition value, when higher products are not formed in any quantity, the relative proportions of the four chlorinated methanes produced were not in accordance with the formula of Martin and Fuchs[16] for a bimolecular step-wise reaction.

The production of chlorinated derivatives of higher paraffin hydrocarbons as observed by Schleede and Luckow in the flaming gases (at high gas rates) is probably the result of thermal dissociation of methane and of chlorinated methanes with subsequent changes of the following types:

$$CH_4 + CH_3Cl \longrightarrow C_2H_6 + HCl,$$
$$CH_2Cl_2 + CH_4 \longrightarrow CH_3CH_2Cl + HCl, \text{ etc.}$$

Also the change in the type of reaction on increasing the gas velocity *may* be due to local development of high temperatures as a result of highly exothermic chlorination. Another possible explanation for the formation of such compounds is indicated by the work of Besson.[17] The latter observed that when chloroform vapors, containing about 1 per cent of iodine, were heated to high temperatures a portion of the chloroform is decomposed yielding compounds such as carbon dichloride (C_2Cl_4), carbon tetrachloride, carbon hexachloride (C_2Cl_6), carbon sesquichloride (C_4Cl_6), hexachlorobenzene, and pentachloroethane. Presumably some such decomposition of chloroform, made during the chlorination of methane, may take place in the presence of chlorine.

All of the four possible chlorinated methanes were obtained by Gault and Benlian[18] on the chlorination of natural gas of Vaux (France), using equal volumes of reactants, in the presence of ferric chloride catalysts in the dark at 245° to 415° C.

The work of Boswell and McLaughlin[19] was directed especially toward the production of maximum yields of methyl chloride from methane by chlorination in the presence of catalysts at about 450° C. Experiments on a small analytical scale were later translated to a larger-scale apparatus in which it was possible to produce 25 grams of methyl chloride per run. The catalyst used throughout these experiments was prepared by impregnating 18 grams of pumice (passing a 12-mesh sieve) with a solution of 10 grams of cupric chloride, $CuCl_2.2H_2O$, in 15 cc. of water, followed by drying at 110° C. and heating in a current of moist nitrogen at 450° C. for 9 hours. This latter treatment effects a reduction to the cuprous condition to the extent of about 75 per cent. A number of factors were examined with regard to their influence on the yield of methyl chloride and the following conclusions were drawn:

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[15] *Ber.*, 1922, 55B, 3710; *Chem. Abs.*, 1923, 17, 2864.
[16] *Z. Elektrochem.*, 1921, 27, 160.
[17] *Compt. rend.*, 1893, 116, 102; *Chem. Soc. Abs.*, 1893, 64 (1), 242.
[18] *Chimie et Industrie*, Special No. (May), 1924, 272; *Chem. Abs.*, 1924, 18, 3109.
[19] *Canad. J. Research*, 1929, 1, 240; *Chem. Abs.*, 1930, 24, 53.

(1) It was found desirable to utilize moist gases in order to maintain the catalyst in a partially reduced and constant condition.

(2) The most favorable reaction temperature was 450° C.

(3) Other factors being equal, the yields of methyl chloride improved as the proportion of the chlorine was reduced.

(4) The effect of diluting the reacting gases with a large volume of nitrogen was found to be advantageous both from the viewpoint of the methyl chloride yield and also in the suppression of explosions.

(5) The best yields of methyl chloride in the presence of the partially reduced cupric chloride-pumice catalysts were obtained under the following conditions: nitrogen to methane ratio of 10:1, and methane to chlorine ratio of 7 or 8:1, using moist gases; reaction temperature of 450° C. In the presence of 8 per cent hydrogen in the methane, the methane to chlorine ratio could be reduced to 3:1. Under these conditions it was found possible to chlorinate methane to methyl chloride with a yield, based on the chlorine used, of 75 to 80 per cent or higher. A small amount of methylene dichloride was also formed.

An attempt was also made by Boswell and McLaughlin to control the chlorination so as to obtain principally carbon tetrachloride. A mixture of pure methane and chlorine in the volume ratio of 1:4 was passed at a rate of 2.5 liters per hour (per 173 grams of cupric chloride on 300 grams of pumice) at 450° C. and gave a 90 per cent yield of carbon tetrachloride. There was no indication of the formation of chloroform or other lower-boiling products but a slight residue boiling above 100° C. was obtained. On doubling the velocity of the reacting gases a series of explosions occurred and these could be suppressed only by diluting the gases with a large quantity of nitrogen. Thus on passing a mixture of 6.28 liters of methane, 26.0 liters of chlorine, and 47.0 liters of nitrogen during 6.5 hours over the catalyst, smooth reaction ensued and the products consisted of 34.5 grams carbon tetrachloride, 3.0 grams of chloroform, and 1.0 gram of higher-boiling liquid. The yield of carbon tetrachloride was thus 80.2 per cent of the theoretical, based on the chlorine.

The employment of catalysts in conjunction with photochemical excitation has been discussed by a number of workers and Tanaka[20] observed that silver chloride was an effective catalyst for the chlorination of methane in the presence of ultraviolet light. The catalytic chlorination and bromination of gases rich in methane hydrocarbons has also been investigated by Zapan.[21]

PHOTOCHEMICAL CHLORINATION

The chlorination of methane is a remarkable example of a reaction powerfully activated by light radiation. Sunlight, diffused daylight, light from a carbon arc, from a metallic filament, and from a mercury vapor lamp have been recommended to promote the chlorination process. In most cases, photochemical combination may be effected at room temperature or even at lower temperatures if methyl chloride is desired, while the reaction may become explosive if the illumination is not carefully controlled.[21a]

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[20] *J. Chem. Ind. (Japan)*, 1921, 24, 789; *Chem. Abs.*, 1922, 16, 1309.

[21] *Thèses Fac. Sci. Univ. Paris*, 1930, 9-99; *Chem. Abs.*, 1932, 26, 77.

According to Bedford, blue light is by far the most effective and though many investigators have suggested ultraviolet light as a suitable activating influence, it is by no means certain that the active radiation is necessarily in the ultraviolet range of wave length.

The marked influence of sunlight on the combination of chlorine and methane was shown as early as 1840 by Dumas,[22] who observed that although methane and chlorine could be mixed in all proportions in the dark without evidence of immediate reactions, exposure of 3 volumes of chlorine and 1 volume of methane to daylight, even when diffused, resulted in a violent explosion. Dilution of this reaction mixture with a volume of carbon dioxide equal to that of the methane suppressed explosive reaction and the combination proceeded smoothly with the formation of carbon tetrachloride and smaller amounts of chloroform. The explosive reaction of methane with chlorine in bright daylight was also noticed by Bischoff[23] and Berthelot[24] but, on the other hand, Phillips[25] reported that a mixture of chlorine and methane could be exposed over water to bright sunlight without appreciable reaction. These differences in results are possibly explicable on the basis of the influence of foreign substances on chain processes in general.

Baskerville and Riederer[26] studied the photochemical chlorination of natural gas. Radiation from a "Uviol" ultraviolet lamp was found, contrary to a number of statements in the literature, to effect no noticeable reaction. However, the remarkable observation was made that light from either an unscreened carbon arc or from the arc screened with blue greatly accelerated the combination but the interposition of green, yellow, or red screens almost immediately decreased the rate of chlorination. Reimposition of the blue screen again accelerated the combination. It appears from this work that the blue radiation is the most effective activating influence and that red, yellow, and green exerted little influence. In further experiments, Baskerville and Riederer obtained yields of 20 to 25 per cent of chloroform and carbon tetrachloride by exposing a heated mixture of chlorine and natural gas to the excitative influence of light from an iron arc.

The influence of the light from a mercury vapor lamp on the combination of chlorine and methane at temperatures of 80° to 100° C. was investigated by Tolloczko and Kling.[27] No explosions occurred even when equal volumes of chlorine and hydrocarbon gas were used. Using a natural gas-chlorine ratio of 1:2, and a gas rate of 4 liters per hour, the relative proportions of the chlorinated methanes formed were as follows: methyl chloride, 16 per cent; methylene chloride, 37 per cent; chloroform, 38 per cent; and carbon tetrachloride, 10 per cent. Besides these products, various chloro-derivatives of ethane were produced, including the solid hexachloroethane.

The work of Bedford[28] on the chlorination of natural gas at low temperatures in the presence of illumination from a white flame arc is of considerable interest. The stepwise nature of the chlorination process was demonstrated by adding the chlorine in small increments to the natural gas confined over water at room temperature when the lower chloro-derivatives were first produced. In order to obtain better control of the reaction and to suppress the formation of carbon tetrachloride, the chlorination was initiated (by means of a white flaming arc) in a gas mixture containing 12.5 per cent of chlorine in an apparatus so arranged that combination occurred in interstices between cakes of ice. The hydrocarbon gas and chlorine were then admitted at regular intervals as the reaction proceeded. The products obtained in this way consisted of 166 cc. of a mixture of methylene chloride and chloroform from 2.6 cubic feet of natural gas. This method of operation was also studied in a larger wooden reaction chamber, provided with a plate glass window through which illumination from a white flame arc could be effected. In this apparatus, 250 cubic feet of natural gas, consumed at the rate of 14 to 30 cubic feet per hour, yielded several gallons of product consisting of the following proportions by volume of the various chlorinated hydrocarbons: 35 per cent of dichloromethane; 35 per cent of chloroform; 5 per cent of carbon tetrachloride, as well as 20 per cent of chloroethanes. About 14 per cent of the product (consisting of 61 per cent dichloromethane, 28 per cent chloroform, 1.5 per cent carbon tetrachloride, and 6 per cent chloroethanes) had dissolved in the water produced by the melting of the ice blocks.

[21a] The use of ultraviolet radiation in the halogenation of methane was also discussed by Ellis and Wells, "The Chemical Action of Ultraviolet Rays," Chemical Catalog Co., Inc., New York, 1925, 196.

[22] *Ann. chim. phys.*, 1840, (2) 73, 84; *Ann.*, 1840, 33, 187.

[23] *Edinburgh New Phil. J.*, 1840-41, 30, 152.

[24] *Compt. rend.*, 1857, 45, 916.

[25] *Amer. Chem. J.*, 1894, 16, 263.

[26] *J. Ind. Eng. Chem.*, 1913, 5, 5.

[27] *Abhandl. Krakauer. Akad. Wissensch.*, 1912, 52, 295; *Chem. Zentr.*, 1913, 2, 98; *Chem. Abs.*, 1914, 8, 1282.

[28] *J. Ind. Eng. Chem.*, 1916, 8, 1090.

Whiston[29] carried out work on the photochemical chlorination of methane from the viewpoint of the production of methyl chloride. No reaction took place in a mixture containing 2 volumes of methane and 1 volume of chlorine in the dark but a slow combination occurred under the influence of light from an ordinary 60-watt metallic filament lamp, placed 30 cm. away from the reaction vessel. Exposure of equal volumes of chlorine and methane to the action of daylight for 4 hours, followed by arc light for 1 hour, produced only 9 per cent of methyl chloride, calculated on the chlorine, together with higher products which were not examined. The conversion of the chlorine into methyl chloride was increased to 24 per cent by employing an excess of methane (2.8 volumes of methane to 1 volume of chlorine).

The observation of Whiston that the photochemical chlorination of methane is powerfully inhibited by nitrosyl chloride, together with the deviation from the law of photochemical equivalence observed in this reaction by Coehn and Cordes,[30] make it appear that the photochemical reaction is of the chain type. The purely thermal chlorination of methane is also probably of the same nature.

INDUSTRIAL PROCESSES

Thermal Chlorination of Methane

Colin[31] proposed to produce chloromethanes by the reaction of a mixture of methane and the appropriate quantity of chlorine in a heated reaction chamber. The temperature was maintained at 100° to 200° C. for the production of chloroform. The reaction is induced and maintained by the passage of an electric spark discharge. Too high combustion chamber temperatures are stated to result in the dissociation of the products. The gaseous products of reaction are freed from hydrogen chloride by washing with water and the chlorinated products cooled and liquefied.

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[29] *J.C.S.*, 1920, 117, 183; *J.S.C.I.*, 1920, 39, 384.
[30] *Z. physik. Chem.*, 1930, 9B, 1.
[31] U. S. Patent 427,744, May 13, 1890.

Weickel[32] described the chlorination of methane to yield methyl chloride mainly without deposition of carbon by heating a mixture of chlorine (1 volume) and an excess of methane (e.g., 10 volumes) at a temperature not exceeding 400° C. for about 10 seconds. *Porous catalysts*, such as animal charcoal, are stated to assist the reaction and reduce the temperature required to about 350° C., while vessels of quartz, porcelain, earthenware, or glass reduce the tendency for carbon separation and allow the employment of moist gases. The products of the reaction are washed with water to remove hydrogen chloride and the methyl chloride is separated from the excess methane by solidifying at —120° C. at 1 atmosphere pressure or, better, by liquefying at —80° C. and 10.5 atmospheres pressure or at —30° C. and 105 atmospheres pressure. The methyl chloride contains some higher chlorinated products from which it is separated readily by fractional distillation.

A number of processes which relate to the thermal chlorination of methane to yield mainly the monochloro-derivative without carbon deposition have been described by Lacy.[33] The chlorination is effected by passing a mixture of chlorine (1 volume) and a considerable excess of methane (e.g., 10 volumes) through a reaction vessel of quartz or porcelain, heated to a temperature of about 400° C. Even at such high gas rates that the period of exposure of the reacting gases is only a matter of a few seconds practically all the chlorine is consumed and mainly methyl chloride is produced. If less methane is employed, for example, 4 to 6 volumes of methane and 1 volume of chlorine, the reaction heat is sufficient to maintain the reaction temperature without an additional source of heating, but the products do not then consist merely of methyl chloride but contain higher chlorinated products.[34] Lacy later[35] described a method of operation in which a very large excess of methane, namely 15 volumes to 1 volume of chlorine, could be used, thus restricting the chlorination to the monochloro-stage. At the same time the process could be rendered thermally self-supporting. This method of operation consisted in preheating 10 volumes of methane to a temperature of 370° C. and then mixing with 5 volumes of methane and 1 volume of chlorine. No carbon deposition or inflammation of the gases occurs and the resulting mixture, now at a temperature of about 250° C., is passed immediately into the reaction chamber. The heat of reaction is then sufficient to maintain the temperature of the reaction chamber at 400° to 500° C. Only 0.01 per cent, or even less, of the chlorine introduced remains unconsumed. The final form of apparatus described by Lacy[36] consists essentially of a cylindrical iron shell with a lining composed of an "acid tile" brick or of silica. The annular space between the brick and the iron shell is filled with finely ground flint. The reaction products are washed with water to remove hydrogen chloride and the methyl chloride separated by cooling to —80° C. under 10 atmospheres pressure. For the production of higher chlorinated products it is claimed that the reaction can be advantageously carried out in steps, always having present an excess of the particular carbon compound entering the step in question.

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[32] French Patent 474,741, 1914; *J.S.C.I.*, 1915, **34**, 1116.

[33] U. S. Patent 1,111,842, Sept. 29, 1914; *Chem. Abs.*, 1914, **8**, 3839; U. S. Patent 1,242,208, Oct. 9, 1917; *Chem. Abs.*, 1918, **12**, 155; U. S. Patent 1,253,055, Jan. 8, 1918; *Chem. Abs.*, 1918, **12**, 702; Canadian Patent 173,969, 1916; *Chem. Abs.*, 1918, **12**, 155; Canadian Patent 191,543, 1919; *Chem. Abs.*, 1919, **13**, 1909; British Patent 16,194, 1914; *Chem. Abs.*, 1916, **10**. 92; British Patent 101,708, 1916; *J.S.C.I.*, 1917, **36**, 1063; French Patent 480,064, 1916; *Chem. Abs.*, 1917, **11**, 1276; French Patent 483,093, 1917; *Chem. Abs.*, 1918, **12**, 42; Swedish Patent 40,494, 1916; *Chem. Abs.*, 1916, **10**, 1910; Norwegian Patent 27,040, 1916; *Chem. Abs.*, 1916, **10**, 2502; all patents assigned to Roessler and Hasslacher Chemical Co.

[34] U. S. Patent 1,190,659, July 11, 1916; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1916, **10**, 2278.

[35] U. S. Patent 1,263,906, Apr. 23, 1918; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1918, **12**, 1649.

[36] U. S. Patent 1,286,353, Dec. 3, 1918; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1919, **13**, 322.

Carter and Coxe[37] obtained higher chlorinated products by passing a mixture of methyl chloride, methane, and chlorine through a reaction chamber heated to 350° to 650° C. The higher chlorinated products, which, in a typical example, may consist of 80 per cent methylene chloride, 15 per cent of chloroform, and 5 per cent of carbon tetrachloride, are removed by cooling and the residual methane and methyl chloride are recirculated with the continuous addition of a mixture of chlorine and methane in the ratio of 2 volumes of chlorine to 1 volume of methane.

In another vapor-phase halogenation process[38] the hydrocarbons and halogen are mixed and heated in the dark. The temperature for the chlorination of methane is maintained at 380° to 400° C., but progressively lower temperatures are used for higher hydrocarbons (see Chapter 30). The products are said to be monohalogen derivatives, all the halogen is consumed, and no carbon deposition or inflammation occurs.

Wheeler and Mason[39] suggested exposing mixtures of chlorine and methane to a relatively high temperature in packed porcelain tubes for a very short period of heating whereby methyl chloride becomes the principal product of the reaction. The same process may be adapted to the chlorination of methyl chloride to yield mainly dichloromethane. The following example suffices to show the main features of the process. Three volumes methane and 1 volume of chlorine are passed through a packed porcelain tube, externally heated to 800° C., at a space velocity (calculated on volume of unpacked tube) of 5500 reciprocal minutes. This results in the production of about 25 per cent methyl chloride, 15 per cent dichloromethane, 1.5 per cent of chloroform, and 1.5 per cent carbon tetrachloride.

Catalytic Chlorination of Methane

In the processes dealing with the catalytic chlorination of methane it is usually proposed to mix the reactants in the cold and then pass such mixtures over a solid catalyst in the dark. The tendency to result in violent reaction or explosions is reduced by the presence of suitable diluent gases or by the use of excess of methane.

Mallet[40] suggested the production of methyl chloride and other chlorinated derivatives by passing a mixture of methane and chlorine over a catalyst of animal charcoal or other porous material at 30° to 90° C., while MacKaye[41] described a process for the chlorination of methane in a reaction chamber packed with granulated coke (said to prevent carbon formation) and heated to 250° to 600° C., optimum about 400° C. The theoretical proportions of reactants (4 volumes of chlorine to 1 volume of methane) are said to be satisfactory for this process, when carbon tetrachloride is desired, or 3 volumes of chlorine to 1 volume of methane if chloroform is sought. Apparatus in which to conduct this reaction has been fully described by MacKaye.[42]

The use of charcoal as a catalyst for the chlorination of methane or natural gas has also been proposed by Garner and Clayton.[43] Methyl chloride, methylene chloride and chloroform are said to be the main products of the reaction between 5 volumes of natural gas and 3 volumes of chlorine, which are first mixed in the cold in the presence of charcoal and then passed through a chamber packed with charcoal and heated to 300° C. The whole process is carried out in the absence of light.

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[37] U. S. Patent 1,572,513, Feb. 9, 1926; *Chem. Abs.*, 1926, **20**, 1243; Canadian Patent 251,763, 1925; *Chem. Abs.*, 1925, **19**, 3272; both patents assigned to S. Karpen and Bros.

[38] Bataafsche Petroleum Maatschappij, British Patent 338,742, 1929; *Brit. Chem. Abs.* **B**, 1931, 237; Dutch Patent 26,862, 1932; *Chem. Abs.*, 1932, **26**, 4342.

[39] U. S. Patent 1,918,624, July 18, 1933; *Chem. Abs.*, 1933, **27**, 4816; British Patent 342,329, 1929; *Brit. Chem. Abs.* **B**, 1931, 475; both patents assigned to Imperial Chemical Industries, Ltd.

[40] U. S. Patent 220,397, Oct. 7, 1879.

[41] U. S. Patent 880,900, Mar. 3, 1908; assigned to Stone and Webster.

[42] U. S. Patent 1,009,428, Nov. 21, 1911; assigned to Stone and Webster.

The chlorination of methane at temperatures of 150° to 500° C. in the presence of polyvalent metals, such as iron, copper, or antimony, or their salts, has been described by Pfeifer.[44] A mixture of chloro-derivatives is obtained, the proportions of which depend upon the operating conditions.

The employment of some kind of inert porous packing material, such as charcoal, has been described by a number of investigators. Thus, Yoneyama and Ban [45] converted methane to a large extent into methyl chloride by passing a dry mixture of methane and chlorine over a catalyst of animal charcoal and finely divided lime at 250° C.

Curme [46] converted methane into a mixture of chlorinated products by passing a dry mixture of an excess of methane and chlorine, having a chlorine content of 5 to 30 per cent according to the desired products, over heated activated carbon. In Curme's process perfectly dry reagents are used and methyl chloride and dichloromethane are the main products. The prime requirement of the absence of water vapor permits the use of apparatus made of iron or steel. The hydrogen chloride may be recovered in the anhydrous condition. The operation is cyclical in character and the methane, substantially undiluted with nitrogen or other gas, is repeatedly circulated with fresh additions of dry chlorine. Dry methane and dry chlorine are continuously supplied to the apparatus but the methane is always maintained in excess. The reaction is carried out at an elevated temperature in the presence of activated carbon prepared by the Chaney process. The products of the reaction are first water-cooled to condense chloroform and carbon tetrachloride partly and are then compressed and liquefied in a Linde tower. Conditions are arranged in this pressure liquefaction so that substantially all the substances present except the methane are condensed, the excess methane alone being carried forward in a gaseous state. The liquid mixture contains the following substances in varying proportions: hydrogen chloride (b.p. —80° C.), methyl chloride (b.p. —24° C.), dichloromethane (b.p. +42° C.), chloroform (b.p. +61° C.), and carbon tetrachloride (b.p. +78° C.). The mixture is then subjected to fractional separation and rectification. The hydrogen chloride may be adsorbed to yield commercial hydrochloric acid, but generally it is stored in steel cylinders in the anhydrous form.

Chlorination has been effected by passing cold methane and chlorine into a liquid medium of high boiling point, such as a melt of inorganic salts, which may also contain a catalyst consisting of ferric or cupric chlorides.[47] For example, a mixture of 1 volume of chlorine and 2 volumes of methane are passed into molten potassium hydrogen sulphate at 320° C. to furnish mainly methyl chloride. Róka [48] proposed to conduct the chlorination of methane in the presence of an excess of superheated steam (2 to 5 volumes of steam per volume of chlorine) at 400° to 500° C.; and in the presence of catalysts such as a chloride of copper, iron, calcium, or magnesium. The proportions of chlorine and methane used depend upon the degree of chlorination required. For example, a mixture of 25 volumes of methane, 38 volumes of chlorine, and 100 volumes of steam on catalytic treatment at 400° to 500° C. yields 8 per cent of methyl chloride, 13 per cent methylene dichloride, 20 per cent chloroform, and 5 per cent carbon tetrachloride, the yields being based on the chlorine consumed.

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[43] U. S. Patent 1,262,769, April 16, 1918; assigned to Metals Research Co.

[44] British Patent 157,253, 1921; *Chem. Abs.*, 1921, 15, 1905; *cf.* Pfeifer, Mauthner and Reitlinger, *J. prakt. Chem.*, 1919, 99, 239; *Chem. Abs.*, 1920, 14, 401.

[45] Japanese Patent 35,701, 1920; *Chem. Abs.*, 1920, 14, 3428.

[46] U. S. Patent 1,422,838, July 18, 1922; *J.S.C.I.*, 1922, 41, 686A; assigned to Carbide & Carbon Chemicals Corp.

[47] Holzverkohlungs-Industrie A.-G., German Patent 393,550, 1921; *J.S.C.I.*, 1924, 43, 848B.

[48] U. S. Patent 1,723,442, Aug. 6, 1929; *Chem. Abs.*, 1929, 23, 4482; British Patent 186,270, 1921; *Chem. Abs.*, 1923, 17, 289; German Patent 447,494, 1921; *Chem. Abs.*, 1929, 23, 3932; all patents assigned to Holzverkohlungs-Industrie A.-G.

A combination of the photochemical and catalytic methods of procedure for the chlorination of methane has been described by Payne and Montgomery,[49] who propose to employ as a catalyst the porous solid material produced by intensive chlorination of a light paraffinic oil.[50] A mixture of 3 volumes of chlorine and 1 volume of methane are brought into contact with this catalyst at 150° F. in the presence of suitable illumination.

Polanyi and von Bogdandy[51] stated that methyl chloride may be produced by the addition of small amounts of the vapors of sodium, cadmium, or zinc to a mixture of chlorine and methane, while Martin and Lux[52] effected the chlorination of methane in the presence of the vapor of the lower chloride of a polyvalent element capable of yielding a higher chloride, e.g., in the presence of antimony chloride. Sper[53] has described a method of chlorinating saturated hydrocarbons, including methane, in a heated reaction chamber packed with pieces of graphite.

PHOTOCHEMICAL CHLORINATION OF METHANE

A considerable number of processes has been proposed for the photochemical chlorination of methane. Usually sunlight, either direct or diffused, is employed in these processes but ultraviolet radiation or other chemically active rays is also mentioned. Elworthy and Lance[54] proposed the chlorination of methane in the presence of a diluent gas such as nitrogen or carbon dioxide in a series of glass tubes exposed to sunlight or other illumination. Walter[55] described the chlorination of methane in air-cooled glass tubes exposed to light of increasing intensity. Treatment of a mixture of 1 volume of methane and 4 volumes of chlorine is said to yield a mixture consisting of methyl chloride, methylene chloride, and chloroform, and 45 per cent of the chlorine was utilized. The chlorination of hydrocarbons such as methane in the presence of ultraviolet radiation has been reported by Graul and Hanschke.[56] In the process of Bedford and Tallmadge,[57] the reaction is induced in direct and intimate contact with a cooling agent capable of removing halogen acids, e.g., ice blocks, in order to limit the reaction and also to remove the lower chlorinated products by condensation. The main products are said to be methyl chloride and methylene chloride while at higher temperatures, without the cooling effect of the ice blocks, quantities of higher chlorinated products are always formed.

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[49] U. S. Patent 1,520,506, Dec. 23, 1924; assigned to Standard Oil Co.; Canadian Patent 268,301, 1927.

[50] For the preparation of this material see Payne and Montgomery, U. S. Patent 1,453,766, May 1, 1923; assigned to Standard Oil Co.; *Chem. Abs.*, 1923, 17, 2349.

[51] British Patent 289,795, 1927; *Chem. Abs.*, 1929, 23, 847.

[52] U. S. Patent 1,801,873, April 12, 1931; assigned to Dow Chemical Co.; *Chem. Abs.*, 1931, 25, 3357.

[53] U. S. Patent 1,721,873, July 23, 1929; *Chem. Abs.*, 1929, 23, 4482.

[54] French Patent 354,291, 1905; *J.S.C.I.*, 1905, 24, 1083A.

[55] German Patent 222,919, 1909; *Chem. Zentr.*, 1910, 2, 255.

[56] U. S. Patent 1,032,822, July 16, 1912; assigned to Badische Anilin and Soda Fabrik; *Chem. Abs.*, 1912, 6, 2686.

[57] U. S. Patent 1,245,553, Nov. 6, 1917; assigned to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1918, 12, 280.

In the various methods of Snelling,[58] a calm and steady chlorination is induced by varying the intensity of illumination in accordance with the variation in the chlorine content of the reacting gases, the gases containing more reactable constituents being exposed to weaker radiation and *vice versa.* Control of the chlorination process is also enhanced by cooling and also by diluting the reacting gases with inert gases. The products of the reaction contain methylene chloride, chloroform, and carbon tetrachloride.

An apparatus for conducting photochemical chlorination in accord with this principle was devised by Snelling.[59] It consists essentially of an enclosed box, all the sides of which except one (the one nearest the source of illumination) are opaque. The box is fitted with a series of parallel plates composed of transparent material such as glass, quartz, celluloid, or mica and as a source of illumination a mercury vapor lamp or any other type of artificial light, or even sunlight, may be used. As a reactive gaseous mixture passes through the apparatus, it is illuminated by light of gradually increasing intensity. A multiple cell unit, operating on the same principle, is arranged for drawing off condensed products or for preheating the gases or modifying the temperature between different cells and different compartments of the same cell.

Another form of apparatus developed by Snelling is of special value because of the small amounts of glass or other transparent media necessary for its construction. This cell possesses only one transparent side, all the other sides and partitions being of opaque material. The single transparent window is screened or clouded in a suitable manner so that its transparency is progressively increased from the point of entry of the reacting gases, where it is opaque, to the point of exit, where it is quite transparent. The gradation in transparency of this window may be effected either uniformly or in steps.

An apparatus has been described by Brooks, Essex and Ward[60] for the photochemical chlorination of a wide variety of hydrocarbons in presence of actinic light. The chlorination is carried out in an opaque container so that the mixture, or solution, of chlorine in hydrocarbons approaches the source of light gradually and so becomes illuminated by light of steadily increasing intensity. In the process of Riesenfeld,[61] the chlorination of methane is effected under the influence of actinic light in an apparatus designed with safety devices for preventing sudden release of flow of materials, which has a tendency to result in explosions. The products of the process were stated by Riesenfeld to vary with the proportions of reactants. By using equal volumes of chlorine and natural gas a product was obtained containing about 80 per cent of methyl chloride, 10 per cent of methylene chloride, 6 per cent of chloroform, 2 per cent of carbon tetrachloride, and 2 per cent of hexachloroethane.

Leiser and Ziffer[62] described a process for the production of methyl chloride mainly in which a mixture of 1 volume of chlorine and 6 volumes of methane is passed successively through four reaction chambers of increasing size in which the gases are exposed to light from mercury vapor lamps extending axially through the chambers. The addition of small quantities of aqueous vapors and hydrogen chloride to the reacting gases prevents the separation of carbon and the formation of products other than methyl chloride. Only 15 per cent of the chlorine is said to appear in the form of products other than methyl chloride.

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[58] U. S. Patent 1,271,790, July 9, 1918; *J.S.C.I.*, 1918, 37, 607A; U. S. Patent 1,285,823, Nov. 26, 1918; *J.S.C.I.*, 1919, 38, 158A; U. S. Patent 1,325,214, Dec. 16, 1919; *J.S.C.I.*, 1920, 39, 135A; U. S. Patent 1,339,675, May 11, 1920; *J.S.C.I.*, 1920, 39, 476A; U. S. Patent 1,365,740, Jan. 18, 1921; *Chem. Abs.*, 1921, 15, 780; U. S. Patent 1,420,346, June 20, 1922; *Chem. Abs.*, 1922, 16, 2867; *cf.* U. S. Patent 1,421,733, July 4, 1922; *Chem. Abs.*, 1922, 16, 2867.

[59] Snelling, U. S. Patent 1,271,790, July 9, 1918.

[60] U. S. Patent 1,191,916, July 18, 1916; assigned to Gulf Refining Co.

[61] U. S. Patent 1,455,508, May 15, 1923; assigned to The Chemical Foundation, Inc.; *Chem. Abs.*, 1923, 17, 2290; *J.S.C.I.*, 1923, 42, 744A.

[62] U. S. Patent 1,459,777, June 26, 1923; *Chem. Abs.*, 1923, 17, 2886; *J.S.C.I.*, 1923, 42, 952A.

Padovani and Magaldi[62a] studied the conditions for maximum yields of methyl chloride by the photochemical chlorination of methane, using a mercury arc with radiation rich in rays of wave-length of 2530 Ångstrom units. Best yields were obtained by using methane-chlorine volume ratios of from 15 to 1 up to 19 to 1, converting as high as 29 per cent of chlorine to methyl chloride.

The use of the silent electric discharge as an activating agent in the chlorination of methane has been proposed by Pfeifer and Szarvasy.[63]

CHLORINATION OF METHANE BY CHEMICAL REAGENTS OTHER THAN CHLORINE

Hochstetter[64] reported the production of methyl chloride by passing a mixture of 3 volumes of methane and 2 volumes of phosgene over finely divided charcoal at 400° C., and Bosshard, Steinitz and Strauss[65] proposed the use of sulphuryl chloride as a chlorinating agent. By passing a mixture of sulphuryl chloride and methane, in the weight proportions of 16 to 135, through an iron tube containing a catalyst, such as charcoal or metal halides, at 300° to 450° C., 30 to 35 per cent of the methane was stated to be converted into methyl chloride, and 15 to 20 per cent into methylene chloride and chloroform.[66]

Krause[67] effected the chlorination of methane by means of antimony pentachloride at 290° to 350° C. in the presence of refractory clay or pumice with the production of mainly methyl chloride with small amounts of methylene chloride and chloroform. In the presence of catalysts such as the chlorides of copper, iron, or calcium, the reaction temperature may be reduced to 250° C. During the reaction, the antimony pentachloride is dechlorinated to the trichloride, which is recovered and rechlorinated in a separate stage. A similar two-stage chlorination process has been described by Tizard, Chapman, and Taylor,[68] who proposed the use of cupric chloride on pumice at a temperature of 500° C., or lower, to convert methane into a mixture of chlorinated derivatives. The dehalogenated copper salt is chlorinated for re-use. It is necessary to exclude oxygen from the chlorinating gases.

Several processes have been described in which hydrogen chloride and oxygen are used as sources of nascent chlorine for the chlorination of methane. Thus, Krause and Róka[69] reported a 60 to 80 per cent yield of chloromethanes, based on the hydrogen chloride used, by treatment of a mixture of methane, hydrogen chloride, and oxygen at 300° to 650° C., and preferably 450° to 550° C., in the presence of catalysts such as active carbon, cupric chloride, ferric chloride, thallic chloride, alkaline earth chlorides and rare earth chlorides. Krause and Róka[69a] prevented the formation of hydrogen chloride in the chlorination

[62a] *Giorn. chim. ind. applicata,* 1933, **15**, 1; *Chem. Abs.*, 1933, **27**, 3443.

[63] U. S. Patent 1,012,149, Dec. 19, 1911; *Chem. Abs.*, 1912, **6**, 459; German Patent 242,570, 1910; *Chem. Abs.*, 1912, **6**, 2211.

[64] Austrian Patent 70,733, 1915; *Chem. Abs.*, 1916, **10**, 1254; German Patent 292,089, 1914; *Chem. Abs.*, 1917, **11**, 1520.

[65] German Patent 413,724, 1921; assigned to Electrochemische Werke G.m.b.H.; *J.S.C.I.*, 1925, 864B.

[66] The combination of phosgene with methane to yield mainly methyl chloride has been ascribed to the action of dilute chlorine; the same is probably true of the reaction with sulphuryl chloride.

[67] U. S. Patent 1,677,831, July 7, 1928; British Patent 195,345, 1922; assigned to Holzverkohlungs Industrie A.-G.

[68] British Patent 214.293, Dec. 14, 1922; *Chem. Abs.*, 1924, **18**, 2523.

[69] U. S. Patent 1,654,821, Jan. 3, 1928; assigned to Holzverkohlungs-Industrie A.-G.; *Chem. Abs.*, 1928, **22**, 966.

[69a] U. S. Patent 1,591,984, July 13, 1926; *Chem. Abs.*, 1926, **20**, 3171; German Patent 478,083, 1923; *Chem. Abs.*, 1929, **23**, 4228; both patents assigned to Holzverkohlungs-Industrie A.-G.

of methane by the addition of oxygen to the mixture, together with diluents such as steam, carbon dioxide or nitrogen. Ernst and Wahl[70] converted methane into chloromethanes by treatment of that hydrocarbon with a mixture of hydrogen chloride and oxygen at 300° to 450° C. in the presence of cupric chloride as a catalyst. These processes, in which hydrogen chloride is utilized as a source of chlorine, would appear to possess considerable technical possibilities provided chlorination is sufficiently controllable at the rather high temperatures essential to such procedure.

Gremli[71] described a process for the chlorination of hydrocarbons such as methane, ethane, or benzene in which a mixture of the hydrocarbon and chlorine, together with oxygen and, if desired, hydrogen chloride and other gaseous diluents, is passed at 300° to 650° C. over catalysts, such as iron, thallium, alkaline earth and rare earth chlorides, or charcoal.

INDUSTRIAL POSSIBILITIES OF THE METHANE CHLORINATION

The results of many investigators indicate the possibility, starting with chlorine and methane, of synthesizing mixtures of chloromethanes either catalytically or in a purely thermal manner without the aid of contact materials. The difficulties inherent in the chlorination process become more pronounced when an attempt is made to effect the reaction on a large scale. The very highly exothermic nature of the process together with the corrosive nature of the reactants and products present difficulties, though they may not be insuperable, in large scale application. At present it does not appear feasible to control the reaction so that only one product is obtained, though in some instances it seems possible to produce a preponderance of one of the chlorinated derivatives. The production of methyl chloride together with only relatively small proportions of higher chlorinated substances has been achieved, while complete chlorination to carbon tetrachloride may also be accomplished though the latter process presents considerable technical difficulties on account of the high heat evolution and the necessity of employing large proportions of chlorine in the reacting mixture, under which conditions the tendency for the explosive reaction, $CH_4 + 2Cl_2 \rightarrow 4HCl + C$, to occur is greatly increased. On the other hand, no methods apparently have been described for controlling the process so as to result in the production of dichloromethane or chloroform in relatively pure state.

For the optimum yield of methyl chloride a considerable excess of methane over chlorine and a fairly high reaction tube temperature (with or without porous packing material) appear to be required, but for the manufacture of carbon tetrachloride principally, an excess of chlorine over methane is necessary in conjunction with active catalysts. In the latter case, the explosive tendency exhibited by the reaction mixture may be suppressed by the addition of a diluent gas such as carbon dioxide or nitrogen. Most of the processes which have been given a large scale trial appear to yield a mixture of chloromethanes. Numerous processes employing light energy as the accelerating agency have been suggested but none has attained any commercial success, probably owing to the difficulty of controlling such photochemical reactions.

Little information is available as to the extent to which the chlorination of methane has been utilized industrially to yield various chloromethanes, but the indications are that the method has not yet achieved a very extensive application. This is probably to be ascribed to the perfection of the existing methods for making chloroform and carbon tetrachloride and to the economy in chlorine consumption which the latter processes present. It is known, however, that methyl chloride is being manufactured from methane for industrial purposes by a number of concerns in the United States.

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[70] German Patent 486,952, 1922; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, 24, 1393.

[71] Austrian Patents 108,421, 1924, and 108,424, 1924; *Brit. Chem. Abs.* B, 1930, 50.

The products produced by the chlorination of methane (or natural gas containing large proportions of methane) consist of the four chloromethanes, all of which have important industrial applications, besides large amounts of hydrogen chloride which may be marketed either as hydrochloric acid or in the anhydrous state.[72] From the economic standpoint, however, it would appear that a very cheap source of chlorine, as well as of methane, would need to be available in order to render the industrial production of the various chloromethanes (the more important of which can be synthesized cheaply in other ways) a commercial success. In particular, the production of carbon tetrachloride by chlorination involves the consumption of the maximum amount of chlorine, while this substance is by far the cheapest of the chlorohydrocarbons.[73]

PROPERTIES AND USES OF THE CHLOROMETHANES

Methyl chloride, CH_3Cl, is a colorless gas of ethereal odor which burns with a white flame. It boils at —24° C. at 760 mm., and dissolves in water to the extent of 4 volumes per volume of solvent and in alcohol to the extent of 35 volumes. The chief industrial application of this substance is as a refrigerant, for which purpose it possesses, in common with ethyl chloride, a particular value.[74] However, care must be taken in its utilization for refrigeration since a number of cases of asphyxiation caused by this gas have been reported.[75] It is also a possible source of methanol, which can be obtained by hydrolysis with steam in the presence of a catalyst. Actually, however, the reverse process, namely, the esterification of methanol by means of dry hydrogen chloride, has been utilized for its manufacture.[76]

The chlorination of methyl chloride is of interest in showing the cumulative nature of the chlorination of methane.[77] Pease and Walz,[78] for example, have shown that methyl chloride undergoes thermal chlorination at approximately twice the rate of methane. The products of the chlorination consist, as might be expected, of all the other three chloromethanes. By suitable adjustment of the conditions it has been found possible to stop the chlorination process principally at one stage. The thermal chlorination of methyl chloride to dichloromethane and to chloroform at temperatures up to about 500° C. has been described by the I. G. Farbenindustrie A.-G.[79] and by Carter and Coxe,[80] while Damoiseau[81] obtained chloroform by passing a mixture of methyl chloride and chlorine over active charcoal at 280° to 350° C. Mason and Wheeler[82] have shown that it is possible to chlorinate methyl chloride mainly to dichloromethane by the purely thermal method at high temperatures and high space velocities. Thus by passing a mixture of 1 part of chlorine and 5.4 parts of methyl chloride through a packed porcelain tube at a space velocity of 1660 reciprocal minutes and at 600° C. a 17.2 per cent conversion of methyl chloride to dichloromethane took place with the formation of only a trace of higher chloro compounds. The yield of dichloromethane based on the chlorine input was 96 per cent of the theoretical.

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[72] It has been proposed to utilize the anhydrous hydrogen chloride produced in chlorination processes for the manufacture of alkyl chlorides from alcohols. I. G. Farbenindustrie A.-G., British Patent 283,877, 1928.

[73] Ethylene dichloride, which can be employed in the place of carbon tetrachloride in some instances, is cheaper on a gallon basis than carbon tetrachloride. For the production of ethylene dichloride, see Chapter 20.

[74] Henning, *Proc. Fourth Int. Congress of Refrigeration*, 1924, 1, 792. Kuenzli (U. S. Patent 1,808,604, June 2, 1931; assigned to Servel, Inc.; *Brit. Chem. Abs.* B, 1932, 84) suggested a refrigerant composition consisting of methyl chloride with 0.05 to 5 per cent of acraldehyde.

[75] Schwartz and Zanger, *Zentral. Gewerbehyg. u. Unfallverh.*, 1926, 3. 246; *Chem. Abs.*, 1927, 21, 2946.

[76] Douane, U. S. Patent 777,406, Dec. 13, 1904; *J.S.C.I.*, 1905, 24, 455. I. G. Farbenindustrie A.-G., German Patent 503,716, 1927; *Chem. Abs.*, 1930, 24, 5768; British Patent 283,877, 1928; *Brit. Chem. Abs.* B, 1928, 886.

[77] In this connection it may be noted that Mason (*Nature*, 1932, 129, 97; *Chem. Abs.*, 1932, 26, 2696) has suggested that the more rapid chlorination of methyl chloride as compared with that of methane may be due to the four hydrogen atoms of methane not being equivalent. Brindley and Lowery (*Phil. Mag.*, 1931, 12, 945; *Chem. Abs.*, 1932, 26, 893), on the other hand, from a study of the refractivities and optical dispersions of methane and its substituted chlorine derivatives conclude that their results did imply the equality of the four carbon to hydrogen linkages in methane. Also as pointed out by Hass (private communication) the substitution of one hydrogen in methane by chlorine may affect the other three carbon to hydrogen linkages and this accounts for the more rapid chlorination of methyl chloride as compared with methane.

[78] *J.A.C.S.*, 1931, 53, 3728.

Dichloromethane (methylene chloride), CH_2Cl_2, is a colorless liquid of chloroform-like odor, boiling point 41° C., and d^{15} 1.337. Besides being an important product of the controlled chlorination of methane and methyl chloride it may be conveniently prepared, in 70 per cent yield, by the reduction of carbon tetrachloride with the theoretical amount of alkaline ferrous salt.[83] It may be separated from methyl chloride by fractional distillation or by hydrolysis of the latter with lime.[84]

The stability of methylene chloride under various conditions has been investigated by Carlisle and Levine.[85] This chlorohydrocarbon was found to be stable to heat up to 120° C. Small quantities of water did not affect its stability at temperatures below 100° C.; the presence of an excess of water brought about no decomposition at its boiling point, but at higher temperatures some decomposition did take place. Pure oxygen or air had only a slight effect up to 120° C. Various metals, such as soft steel, aluminum, copper, tin and lead were not corroded by either dry methylene chloride or the chloride saturated with water up to 140° C. Brass, however, was attacked at 60° C. Methylene chloride appears to be the least corrosive of the higher chlorinated hydrocarbons and its corrosive effect is hardly greater than that of water. Davenport[85a] suggested the addition of a base to inhibit the reaction of refrigerants such as methylene chloride with water. Methylene chloride and other chlorinated hydrocarbons are also said to be rendered more stable by the presence of a small quantity of amylene.[85b] Chloroform, as well as carbon tetrachloride, hexachloroethane, trichloroethylene and other chlorinated hydrocarbons may be stabilized by the addition of oil-soluble azo-dyes such as amino-azobenzene, according to Zuckermandel.[85c] Alkylamines have also been suggested[85d] for preventing or reducing the decomposition of liquid chlorinated hydrocarbons.

Methylene chloride is a valuable solvent for fats, oils or resins, but it must always be used with caution and in well-ventilated rooms. This substance, as well as dichloroethylene, has been suggested as a refrigerant for air-conditioning plants.[86]

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[79] British Patent 283,119, 1927; *Chem. Abs.*, 1928, **22**, 3893; French Patent 646,661, 1927; *Chem. Abs.*, 1929, **23**, 2191.

[80] U. S. Patent 1,572,513, Feb. 9, 1926; assigned to Karpen and Bros.

[81] *Compt. rend.*, 1880, **91**, 1011.

[82] *J.C.S.*, 1931, 2282.

[83] Soc. chim. des usines du Rhône anciennement Gilliard, Monnet et Cartier, British Patent 225,174, 1923; *Chem. Abs.*, 1925, **19**, 1866.

[84] Weber and Erasmus, U. S. Patent 1,565,345, Dec. 15, 1925; assigned to T. Goldschmidt A.-G.

[85] *Ind. Eng. Chem.*, 1932, **24**, 146.

[85a] U. S. Patent 1,809,833, June 16, 1931; assigned to Chicago Pneumatic Tool Co.; *Chem. Abs.*, 1931, **25**, 4638.

[85b] Harris, U. S. Patent 1,904,450, April 18, 1933; *Chem. Abs.*, 1933, **27**, 3481; German Patent 562,820, 1932; *Chem. Abs.*, 1933, **27**, 992; both patents assigned to Roessler and Hasslacher Chemical Co.

[85c] U. S. Patent 1,819,585, Aug. 18, 1931; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 216.

[85d] Imperial Chemical Industries, Ltd., French Patent 744,128, 1933; *Chem. Abs.*, 1933, **27**, 3941.

[86] Waterfill, *Ind. Eng. Chem.*, 1932, **24**, 616.

It has also been suggested as a solvent for the dewaxing of lubricating oils since it dissolves only very small quantities of wax at low temperatures and is still miscible with the oils in all proportions.[87] Other advantages claimed for its use follow. (1) The wax cake, after filtering, can be freed of oil by washing with methylene chloride and therefore fractional melting and sweating need not be resorted to as in the usual dewaxing processes to free the wax of oil. (2) The rate of chilling is not an important factor as when solvents such as naphtha are used, since with the latter solvents too rapid chilling may cause difficulties in the filtration operation. (3) Dewaxing and chilling may be carried out in one operation by reducing the pressure, whereby part of the methylene chloride is evaporated, thus lowering the temperature of the remaining liquid.

The progressive chlorination of methylene chloride to yield chloroform and carbon tetrachloride has been described by Lacy.[88] Six volumes of methylene chloride and 1 volume of chlorine are led in gaseous form through a reaction vessel maintained at 350° to 450° C.

On treatment of dichloromethane (methylene dichloride) with ammonia, hexamethylenetetramine [$(CH_2)_6N_4$] results, according to Carter.[88a] The condensation of dichloromethane with phenols in the presence of ammonia (apparently through the intermediate formation of hexamethylenetetramine) to form synthetic resins has been described by Coxe and Carter.[88b]

Chloroform, $CHCl_3$, because of its use as an anesthetic and also as a solvent and extraction agent for ethereal oils, fats, resins, rubber, sulphur, and some of the alkaloids, is an important chlorinated derivative of methane. It may be produced not only by the chlorination of methane but also by other well-known methods. In the United States a common method of preparation is the reduction of carbon tetrachloride by means of finely divided iron in the presence of dilute acid, a process which proceeds smoothly to the chloroform stage.[89] The Soc. chim. des usines du Rhône[90] reported that the reduction of carbon tetrachloride to chloroform can be accomplished with 90 per cent yield by treatment with a warm alkaline ferrous salt. Chloroform is a heavy colorless liquid of boiling point 61.2° C. and d_4^0 1.5264.

Carbon tetrachloride, CCl_4, is a colorless heavy liquid of boiling point 76.7° C. at 760 mm. It finds very extensive application as a solvent for resins, fats, bitumens, etc. It is a solvent for asphalts, refined bitumens, rubber, most natural gums, but not for cellulose esters, celluloids, gum arabic or gum tragacanth. Carbon tetrachloride and dichloroethane (ethylene dichloride) have been suggested by Britton[90a] as solvents for the extraction of o-hydroxydiphenyl (o-phenylphenol) from alkaline solutions of the crude product. It is produced industrially on a very large scale by the chlorination of carbon disulphide in the presence of a catalyst, such as sulphur chloride[91] or iodine.[92] It may also be produced by passing chlorine through a mass of incandescent coke.[93] Although used considerably as a cleansing agent and solvent it does possess toxic qualities[94] and also tends to liberate hydrochloric acid slowly in the presence of water; when dry it is non-corrosive to iron, nickel, and aluminum. Another of its important applications is as a component of fire-extinguishing solutions or emulsions, in conjunction with emulsified carbon dioxide solutions, etc. Unfortunately it tends to decompose, liberating hydrogen chloride and chlorine when exposed to burning materials in the presence of water-vapor. This tendency to decompose under such conditions may be partly suppressed by the addition of various chemical agents.

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[87] Carlisle and Levine, *Ind. Eng. Chem.*, 1932, **24**, 384.

[88] Canadian Patent 191,543, 1919; *Chem. Abs.*, 1919, **13**, 1909.

[88a] U. S. Patent 1,635,707, July 12, 1927; *Chem. Abs.*, 1927, **21**, 2906; British Patent 252,609, 1925; *Chem. Abs.*, 1927, **21**, 2273; both patents assigned to S. Karpen and Bros.

[88b] U. S. Patent 1,566,823, Dec. 22, 1925; *Chem. Abs.*, 1926, **20**, 484; British Patent 220,985, 1923; *J.S.C.I.*, 1924, **43**, 953B; both patents assigned to S. Karpen and Bros.

[89] Smith, U. S. Patent 753,325, March 1, 1904; Griswold and Strosacker, U. S. Patent 1,101,025, June 23, 1914.

[90] British Patent 225,174, 1924; *J.S.C.I.*, 1925, 613B. See also, Bellone, U. S. Patent 1,627,881, May 10, 1927; *Chem. Abs.*, 1927, **21**, 2136.

[90a] U. S. Patent 1,835,755, Dec. 8, 1931; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 220.

[91] Baillio, U. S. Patent 1,260,622, March 26, 1918; for separation from sulphur compounds see Baillio, U. S. Patent 1,260,621, March 26, 1918.

[92] Cote, French Patent 327,322, 1902; Febvre, French Patent 355,423, 1905.

[93] Maywald, U. S. Patent 870,518, Nov. 5, 1907.

Because of their high specific gravities carbon tetrachloride as well as chloroform and tetrachloroethylene have been suggested as solvents for dewaxing operations in which the wax or solid paraffin and chilled oil are separated by centrifugal methods.[94a] The chlorinated hydrocarbon, in which the wax is insoluble or only slightly soluble, is added to the chilled oil in such a quantity as to produce a mixture of hydrocarbon and halogenated hydrocarbon which possesses a higher specific gravity than the wax. If necessary the viscosity of the mixture may be diminished by the addition of a light hydrocarbon.

According to Daur,[94b] carbon tetrachloride reacts with methane to form compounds such as chloroform, tetrachloroethylene, carbon, hydrogen chloride and hexachloroethane. Bartlett[95] prepared hexachloroethane by treating carbon tetrachloride with aluminum and aluminum chloride at a temperature of about 60° to 75° C.

ACTION OF OTHER HALOGENS ON METHANE

Very little work on the *bromination* of methane has been reported and only a few processes have been described dealing with this subject. The bromination of the higher paraffins appears to take place with much greater difficulty than chlorination and also there is less tendency for polysubstitution products to be formed. From the standpoint of toxicity, Henning[95a] found methyl bromide safe to use as a refrigerant or fire extinguisher. Kudicke and Weise[95b] observed that bromoform, tetrachloroethane, dibromoethylene, and in high concentrations, tetrachloroethylene, proved effective germicides in vapor form.

According to Schroeter,[96] methyl bromide may be produced by passing a gaseous mixture of bromine and methane over a catalyst at temperatures above 200° C. The catalysts suggested comprise iron, copper, copper bromide, nickel, cobalt, or salts of these metals and their mixtures, and, in general, of compounds of polyvalent metals. An excess of methane is said to favor the production of methyl bromide, while methylene bromide and bromoform are also formed if higher bromine concentrations and higher temperatures are employed.

In the process developed by Bosshard, Steinitz, and Strauss[97] a gaseous mixture of bromine and methane is subjected to a temperature of 300° to 450° C. at atmospheric pressure, or at higher pressures, in the absence of active catalytic agents. Thus, on passing a mixture of 1 part of methane and 12 parts of bromine through a quartz tube at 400° C. about 3.1 parts of methylene bromide and 3.1 parts of bromoform, as well as small amounts of carbon tetrabromide, are produced. It is maintained that by varying the concentration of the reactants, any of the four bromo-derivatives may be produced in predominating amount.

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[94] An editorial discussion of toxic qualities of chlorinated hydrocarbons, particularly carbon tetrachloride, is found in *Ind. Eng. Chem.*, 1932, 24, 716. The toxic qualities of the halogen derivatives of methane, ethane and ethylene have been investigated by Lazarev, *Arch. exptl. Path. Pharmakol.*, 1929, 141, 19; *Chem. Abs.*, 1931, 25, 3074; and by Henderson, *Arch. intern. pharmacodynamie*, 1930, 38, 150; *Chem. Abs.*, 1932, 26, 2511.

[94a] Bergedorfer Eisenwerk A.-G., Astra Werke, German Patent 535,274, 1926; *Chem. Abs.*, 1932, 26, 1113.

[94b] *Ges. Abhandl. Kenntnis Kohle*, 1932, 10, 155; *Chem. Zentr.*, 1932, 2, 2032; *Brit. Chem. Abs.* A, 1933, 254.

[95] U. S. Patent 1,800,371, April 14, 1931; *Chem. Abs.*, 1931, 25, 3362.

[95a] *Chemistry and Industry*, 1933, 462.

[95b] *Arch. Schiffs-Tropen Hyg.*, 1926, 30, 231; *Chem. Abs.*, 1926, 20, 3307.

[96] German Patent 330,642, 1917; *J.S.C.I.*, 1921, 40, 280A.

[97] German Patent 391,745, 1921; assigned to Elektrochemische Werke; *J.S.C.I.*, 1924, 43, 811B.

The direct iodination of methane by elemental iodine has not been reported. The only industrially important iodomethane, namely iodoform, CHI_3, can readily be prepared by the action of iodine in alkaline solution on many alcohols, ketones, and aliphatic oxygenated compounds. It is interesting to note that the iodine atoms in many iodomethanes may be replaced by the other halogens by direct treatment with the halogen. Thus bromiodomethane, CH_2BrI, may be obtained by the action of a limited quantity of bromine, or better of iodine bromide, on diiodomethane, while chlorobromomethane, CH_2BrCl, is produced by treatment of chloriodomethane with bromine.[98]

FLUORINE DERIVATIVES OF METHANE

The direct combination of fluorine and methane occurs with explosive violence. Moissan[99] found that, on passing a current of fluorine through a platinum tube into an atmosphere of methane, a violent reaction occurred, accompanied by incandescence and carbon deposition. A mixture of fluoromethanes was obtained from which he was able to isolate carbon tetrafluoride. Even at very low temperatures the reaction takes place with extreme violence, for Moissan and Chavanne[100] found that solid methane at —187° C. combined with liquid fluorine with a bright flash and an explosion.

Although the simple fluoromethanes are of no industrial importance, certain mixed fluorochloro compounds are attracting much attention from the viewpoint of their use as refrigerants, particularly the *dichlorodifluoromethane,* CCl_2F_2, which has been developed for this purpose by Midgley.

It is essential that a medium for mechanical refrigeration should be stable, and non-corrosive, and possess suitable vapor-pressure characteristics. In addition, when certain special cases are contemplated, non-toxicity and non-inflammability become of equal importance. It has been shown that dichlorodifluoromethane fulfills these conditions to an unusual degree.

PREPARATION AND PROPERTIES OF DICHLORODIFLUOROMETHANE

The pioneer work of F. Swarts[100a] supplied the basis for the large scale manufacture of dichlorodifluoromethane, which is carried out by treating carbon tetrachloride with pure dry (sublimed) antimony trifluoride in the presence of a small amount of antimony pentachloride as catalyst. The reaction may be represented as follows:

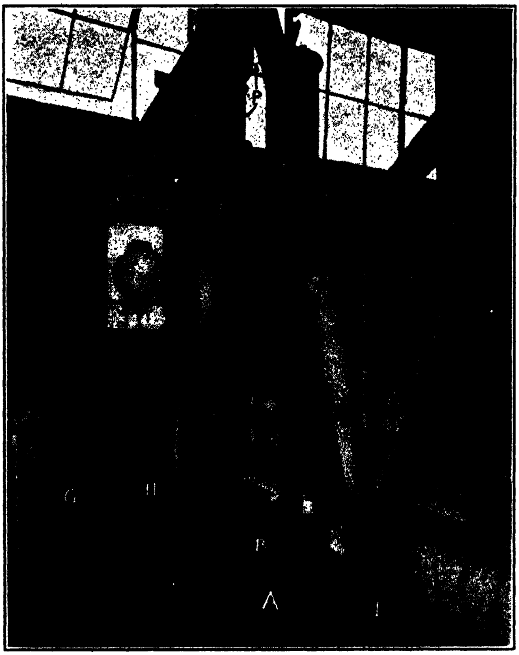
$$3CCl_4 + 2SbF_3 \xrightarrow{(SbCl_5)} 3CCl_2F_2 + 2SbCl_3$$

and although small amounts of trichlorofluoromethane are formed, under suitable conditions the yield of CCl_2F_2 may be as high as 94 per cent of the theoretical. The apparatus, described by Midgley and Henne[101] for carrying out this process, is represented in Figure 26, and consists essentially of a steam-jacketed autoclave, *A,* with loading hole, *B,* and a dump valve at bottom. *C* is a flat spiral fraction-

[98] Henry, *Compt. rend.*, 1886, 101, 599; *Chem. Soc. Abs.*, 1886, 50, 43.
[99] *Compt. rend.*, 1890, 110, 952.
[100] *Compt. rend.*, 1905, 140, 409.
[100a] The numerous contributions of Swarts are abstracted in *Chem. Abs.*
[101] *Ind. Eng. Chem.*, 1930, 22, 542.

ating column made from monel metal; *D* is a monel metal dephlegmator. The pipe, *P*, leads the gases escaping from the dephlegmator to the washer, *F*, in which a caustic solution eliminates any traces of phosgene, chlorine, or any derivative of pentavalent antimony. From there the gases pass through a regulating valve to the gasometer, *G*, and thence to pump, *H*, which delivers the liquefied product to receivers located on a lower level.

The operation is as follows: 125 pounds of sublimed antimony trifluoride is delivered to the autoclave through *B*, and the required amount of antimony pentachloride is added. Hole *B* is closed, the carbon tetrachloride supply pump, *I*, is started, and steam is turned on. The reaction starts immediately and in a short while the pressure reaches 60 pounds; the subsequent operation is automatic. The end point is very sharp and corresponds to the theoretical quantity of tetrachloride. The pressure is then released through a by-pass valve on the pressure-regulating system. The dump valve is opened and the molten antimony trichloride flows by gravity into hooded containers. No further cleaning is required. After the dump valve is closed the apparatus is ready for the next run.



Courtesy Industrial and Engineering Chemistry

FIG. 26.—Apparatus for Production of Dichlorodifluoromethane.
A—Autoclave; *C*—fractionating column; *D*—dephlegmator; *F*—washer; *G*—gasometer; *H*—pump.
(Midgley and Henne)

Another method for preparing fluorinated hydrocarbons consists in passing chlorinated hydrocarbons over an alkali or alkaline-earth fluoride at temperatures above 350° C.[101a] For example, carbon tetrachloride reacted with calcium fluoride at 500° C. yields 61 per cent of dichlorodifluoromethane, 35 per cent of trichlorofluoromethane and 4 per cent of unchanged carbon tetrachloride.

The preparation of fluorinated hydrocarbons by the reaction of hydrogen fluoride with aliphatic hydrocarbons or their halogen derivatives, in the presence of antimony trichloride or pentachloride at raised temperatures and pressures, has also been suggested.[101b] Carbon tetrachloride, chloroform, methylene chloride, fluorotrichloromethane, ethyl chloride, isopropyl bromide, ethylene dibromide, tetrachloroethane and similar compounds may be used as starting materials.

The general properties of dichlorodifluoromethane have been described by Midgley and Henne,[102] while a very full account of the general thermodynamic properties of this compound has been given by Buffington, Gilkey, and others.[103]

Dichlorodifluoromethane is a colorless gas having the following physical constants: boiling point, —30° C.; freezing point, —155° C.; density of liquid 1.40—0.00326 t; C_p (liquid), 0.224; C_p (vapor), 0.15; $\frac{C_p}{C_v}$ vapor = 1.124; latent heat, 39 cal. per gram at boiling point and 34 cal. per gram at 30° C.; vapor pressure, $\log p = 4.321 - \frac{1047}{\text{T abs.}}$.

According to vapor-phase tests, the vapor of this compound is stable for at least 30 days at 175° C. if pure and dry and in an unreactive container, i.e., one made of carbon steels and stainless steels, aluminum, copper, monel metal, tin, and tin-lead solders. Water always causes corrosion and decomposition; zinc, magnesium, and water all attack the combined chlorine but not the fluorine. At room temperature, liquid dichlorodifluoromethane is neither decomposed nor corrosive in contact with the ordinary structural materials. The compound is non-inflammable and its fire-extinguishing properties may be gaged by the fact that gaseous mixtures of it and butane, containing as high as 30 per cent butane, are non-inflammable. Table 119a, in which the toxicity of this compound is compared with some of the refrigeration media at present employed, shows that dichlorodifluoromethane is non-toxic from the practical viewpoint of health hazards.

TABLE 119B.—*Comparative Toxicity of Dichlorodifluoromethane and Some Refrigerants.*

(Concentrations in per cent by volume.)

Gas	Kills Animals in Very Short Time	Dangerous to Life in 30–60 Minutes	Maximum for Several Hours Without Danger to Life
Ammonia	0.5–1.0	0.25–0.45	0.01
Methyl chloride	15–30	2–4	0.05–0.1
Carbon dioxide	30	6–8	2–3
Dichlorodifluoromethane	not attainable	80	40

The diagrams (Figs. 27 and 28), which have been made by Midgley and Henne, give an approximate representation of the variation of boiling points of various chloro- and fluorochloro-methanes, and help to demonstrate the superiority of dichlorodifluoromethane for practical refrigeration purposes.

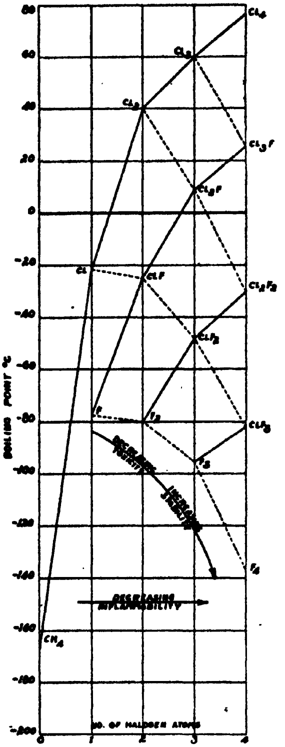
[101a] E. I. duPont de Nemours and Co., Inc., British Patent 390,191, 1931; *Brit. Chem. Abs.* **B**, 1933, 457.

[101b] Kinetic Chemicals, Inc., British Patent 391,168, 1933; *Chem. Abs.*, 1933, **27**, 4813; German Patent 552,919, 1931; *Chem. Abs.*, 1932, **26**, 5967; *cf.* Osswald, Müller and Steinhäuser, German Patent 575,593, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4813.

[102] *Loc. cit.*; also *Ind. Eng. Chem.*, *News Ed.*, 1931, **10** (1), 3.

[103] Buffington and Gilkey, *Ind. Eng. Chem.*, 1931, **23**, 254; Gilkey, Gerard and Bixler, *ibid.*, 1931, **23**, 364; Bichowsky and Gilkey, *ibid.*, 1931, **23**, 366; Buffington and Fleischer, *ibid.*, 1931, **23**, 1290; Buffington and Gilkey, *ibid.*, 1931, **23**, 1292.

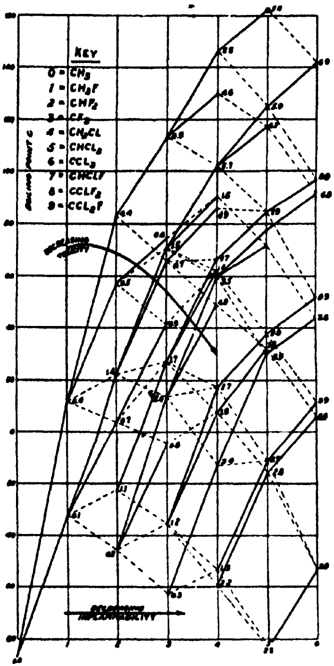
In addition to their use as refrigerants the fluorine derivatives of methane have been proposed as fire-extinguishers and as anesthetics. This applies particularly to those derivatives which are prepared by replacing another halogen element by fluorine in compounds containing at least two halogen atoms. Examples of such substances are dichlorodifluoromethane and trichloromonofluoroethane prepared from carbon tetrachloride and tetrachloroethane, respectively, by treatment with antimony trifluoride in the presence of antimony pentachloride.[104]



Courtesy Industrial and Engineering Chemistry

FIG. 27.—Diagram Showing Boiling Points of Chloro and Fluoro Derivatives of Methane. (Midgley and Henne.)

(Halogens only are indicated. Carbon and hydrogen understood, thus: ClF = CH_2ClF and Cl_4 = CCl_4).



Courtesy Industrial and Engineering Chemistry

FIG. 28.—Flammability of Chloro and Fluorochloro Derivatives of Methane. (Midgley and Henne.)

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[104] Frigidaire Corporation, French Patent 701,324, 1930; *Chem. Abs.*, 1931, 25, 4011. Also Midgley, Henne and McNary, British Patent 357,263, 1930; assigned to Frigidaire Corporation; *Brit. Chem. Abs.* B, 1932, 84. *Cf.* Henne, British Patent 389,619, 1932; *Brit. Chem. Abs.* B, 1933, 457; British Patent 378,324, 1932; *Brit. Chem. Abs.* B, 1932, 1019; both patents assigned to Frigidaire Corp.

Chapter 30

Halogenation of Methane Homologues. Properties and Uses of Halogen Derivatives

As the series of paraffin hydrocarbons is ascended the number of possible halogen-substituted derivatives increases enormously.[1] Direct halogenation of the methane homologues, though it furnishes only a relatively small proportion of the theoretically possible number of products, nevertheless results in the production of a diversity of derivatives so that the difficulties of controlling the process in order to obtain a preponderance of one compound are considerably increased. As in the case of methane, halogenation of the homologues of methane is an exothermic process the control of which often necessitates the use of diluent gases (in the vapor-phase halogenation) or diluent liquids (in liquid-phase operation). Methods of halogenation may be broadly summarized under the general heads of (1) thermal, (2) catalytic, and (3) photochemical, and (4) the use of chemical halogenating agents, other than the halogens themselves.

No general rules appear to apply adequately to the course of halogenation of higher paraffins, though Herzfelder[1a] has proposed the following generalizations:

> "When into a monohalogen compound a second halogen atom is introduced it always attaches itself to that carbon atom which is situated next to the carbon atom already united with halogen. In the case of further substitution, this rule only holds for bromine, of which it is never possible, by other than violent means, to attach more than one atom to each atom of carbon. On the other hand, when a third atom of chlorine is introduced it frequently attaches itself to a carbon atom that is already united with chlorine.
>
> "Bromides that already contain one atom of bromine united with each atom of carbon cannot easily be further brominated; chlorides, however, take up more chlorine. A normal hydrocarbon, when brominated by ordinary means, takes up as many atoms of bromine as it contains atoms of carbon; this was shown in the case of methane, and also, although not with absolute certainty, in that of butane, hexane, heptane and octane."

With respect to the chlorination of hydrocarbons the following generalizations, given by Hass and McBee[2] have been found to hold for propane, normal butane, isobutane, normal pentane and isopentane:

> "1. When a paraffin hydrocarbon is chlorinated either thermally or by the action of light, all of the theoretically possible isomers are formed.
>
> 2. At low temperatures tertiary and secondary hydrogen atoms are substituted more

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[1] Blair and Henze (*J.A.C.S.*, 1932, 54, 1098) calculated the number of stereoisomeric and non-stereoisomeric mono-substitution products of paraffin hydrocarbons. Some of their values for the total number of both stereoisomers and non-stereoisomers of mono-substituted paraffins are as follows:

Carbon Atoms	*Total Isomers*	*Carbon Atoms*	*Total Isomers*
1	1	7	74
2	1	8	199
3	2	10	1,553
4	5	12	12,832
5	11	15	328,092
6	28	20	82,299,275

[1a] *Ber.*, 1893, 26, 2432; *Chem. Soc. Abs.*, 1894, 66, 1.

[2] Private communication from Professor H. B. Hass of Purdue University.

rapidly than primary ones. If the primary hydrogen atoms outnumber the tertiary and/or secondary ones sufficiently (isobutane, isopentane) the primary isomers will predominate at any temperature between 20° and 620° C. At still lower temperatures the tertiary isomer predominates even in the case of isobutane.

3. At 600° C. and above, there is a very close approach to non-selective chlorination, all hydrogen atoms being substituted at the same rate. Thus the yields of primary isomers relative to total monochlorides is approximately 90 per cent for isobutane, 60 per cent for n-butane and 75 per cent for propane.
4. Neither highly moist conditions nor careful drying affects appreciably the ratio of isomeric monochlorides. The same is true of the carbonaceous deposit which forms on the walls of the reaction tube.
5. An unnecessary prolonged reaction time results in appreciable pyrolysis, the tertiary isomers decomposing most rapidly followed in order by the secondary and primary.
6. The ratio by weight of total polychlorides to total monochlorides at any ratio of hydrocarbon to chlorine greater than 1:1 is approximated by the equation $X = KY$ where X is the ratio of monochlorides to polychlorides, K is an empirical constant peculiar for each hydrocarbon and Y is the ratio of moles of hydrocarbon to moles of chlorine in the unreacted gases.
7. A high proportion of primary hydrogen in the hydrocarbon molecule correlates with a high value of K in the above equation.
8. Dichlorination proceeds by two mechanisms: (1) loss of hydrogen chloride and addition of chlorine to the resulting olefin, and (2) progressive substitution.
9. A slow thermal chlorination favors mechanism (1), while a rapid thermal chlorination favors mechanism (2).
10. The presence of chlorine on a carbon atom does not tend to promote further reaction on that carbon atom during the second substitution."

From an industrial standpoint, the chlorination of lower homologues of methane has attracted much attention as a basis for the conversion of these abundant hydrocarbons into the lower aliphatic alcohols. For this purpose it is necessary to control the chlorination process so that monochlorinated products are formed either exclusively or to a preponderating extent. The hydrolysis of such monochlorinated products proceeds smoothly in the presence of alkalies to the corresponding alcohol. Because of the relatively high cost of bromine, bromination processes are of less interest from a commercial point of view, although ethyl bromide has attained a measure of importance in the manufacture of tetraethyl lead. Fluorinated paraffin hydrocarbons have been prepared and described, particularly by Swarts, but only the methane derivatives have been of commercial interest (see Chapter 29). Direct iodination of saturated hydrocarbons has received but little attention.

ETHANE

Thermal Chlorination. Ethane is so much more readily chlorinated than methane that it is possible to chlorinate this hydrocarbon in natural gases containing only 10 per cent of the hydrocarbon, mixed with upwards of 90 per cent of methane, without appreciable formation of chloromethanes.[2a]

For the purely thermal chlorination of ethane a number of investigators have used various contact materials at moderately high temperatures. Thus Jones, Allison, and Meighan[3] found that chlorination of natural gas, containing 10 per cent of ethane, took place at temperatures slightly below 250° C. in the presence of porous charcoal with the production of chlorinated ethanes mainly. The main product of the chlorination of ethane under such conditions was hexachloroethane, C_2Cl_6, but ethyl chloride, dichloroethane, trichloro- and tetrachloro-ethanes were also noted.

[2a] Britton and Prescott (U. S. Patent 1,908,312, May 9, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, 27, 3724) take advantage of this difference in reactivity in purifying methane from ethane and higher hydrocarbons. They proposed to react the mixture of gases with only sufficient chlorine to combine with ethane and the higher hydrocarbons at 200° to 400° C. in the presence of lead chloride.

[3] *U. S. Bur. Mines Tech. Paper*, 255, 1921.

As a method of obtaining principally ethyl chloride Lacy[4] proposed the passage of a gaseous mixture containing chlorine and an excess of ethane (1 volume of chlorine and 8 volumes of ethane) through a reaction chamber maintained at 300° to 500° C. The hydrogen chloride formed during the reaction was removed by washing with water and the ethyl chloride separated from the excess ethane by cooling to a low temperature and condensing; for example to —20° C. and 8 atmospheres pressure. The ethyl chloride obtained by this process can be passed over lime (calcium oxide) at 450° C. to yield ethyl ether.[5]

In still another process the paraffin hydrocarbon and chlorine (or bromine) are mixed in the vapor phase in the dark and heated.[6] In the reaction all of the halogen is used up and no carbonization or flame results; the product is principally the alkyl halide. The temperatures specified are 380° to 400° C. for methane; 360° to 380° C. for ethane; 330° to 380° C. for propane and butane; and 250° to 330° C. for pentane.

Catalytic Chlorination. Tolloczko and Kling[7] chlorinated natural gas in the presence of pumice or pumice impregnated with cupric chloride at temperatures of 400° C. or thereabouts. When chlorine was in excess the preponderating ethane derivative formed was hexachloroethane while in the presence of an excess of natural gas, ethyl chloride, dichloro- and tetrachloro-ethanes were obtained.

A pumice catalyst impregnated with cupric chloride which was reduced partially to the cuprous condition before use was employed by Boswell and McLaughlin.[8] It was found that the procedure followed in the chlorination of methane had to be considerably modified for the chlorination of ethane. Only a few experiments were performed but the yield of ethyl chloride, calculated from the ethane and chlorine used, was at least 75 per cent.

Charcoal, or other porous material, has also been suggested as a catalyst for the chlorination of ethane. For example, Mallet[9] suggested the chlorination of ethane in the presence of animal charcoal at 30° to 90° C. In another process[10] the mixture of halogen gas and excess hydrocarbon gas is caused to react with the liberation of the gaseous halogen acid and the formation of reaction products of higher boiling points than the original hydrocarbon. The gaseous reaction products are then separated from the unchanged hydrocarbon by liquefaction, and the latter is returned to the system for further treatment.

In the process developed by Gremli[11] methane, ethane, or benzene is treated with chlorine at 300° to 650° C. in the presence of oxygen together with hydrogen chloride, if desired. Diluents such as steam, carbon dioxide, or nitrogen may be added to the gaseous mixture. Catalysts such as iron, thallium, alkaline or rare earth chlorides, or charcoal are employed.

Photochemical Chlorination. Frankland and his collaborators employed photochemical chlorination in their early work on the structures of ethane and the other paraffins. Dry ethane and chlorine were mixed in the dark and then exposed to diffused daylight. Using equal volumes of reactants, ethyl chloride was produced;[12] by using two volumes of chlorine to one of ethane, some ethylene dichloride was formed.[13] Chlorination of ethyl chloride with an excess of chlorine in sunlight led to the production of a substance whose odor resembled camphor.[14] Schorlemmer[15] found that ethane from two sources, when treated with an equal volume of chlorine and exposed to diffused daylight at 5° C., yielded ethyl chloride with a small amount of ethylene dichloride. The same products were obtained when using dry and also moist gases and the chlorination reaction served to demonstrate the identity of ethanes synthesized in different ways. Similarly, Darling[16] obtained ethyl chloride and ethylene dichloride by exposure of an equimolecular mixture of ethane and chlorine to the influence of diffused daylight. The photochemical chlorination of natural gas under the influence of ultraviolet light at 80° to 100° C. was found by Tolloczko[17] to proceed smoothly without explosion when using equal volumes of chlorine and natural gas. Besides chloromethanes, di- and tetrachloroethanes were formed, as well as hexachloroethane when an excess of chlorine was employed.

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[4] U. S. Patent 1.242,208, Oct. 9, 1917; assigned to Roessler and Hasslacher Chemical Co.; *J.S.C.I.*, 1917, **36**, 1248.

[5] Lacy, U. S. Patent 1,245,742, Nov. 6, 1917; assigned to Roessler and Hasslacher Chemical Co.; *J.S.C.I.*, 1918, **37**, 20A.

[6] Bataafsche Petroleum Maatschappij, British Patent 338,742, 1929; *Brit. Chem. Abs.* **B**, 1931, 237. Also Dutch Patent 26,862, 1932; *Chem. Abs.*, 1932, **26**, 8342.

[7] *Abhandl. Krakauer Akad. Wissensch.*, 1912, **52**, 295; *Chem. Zentr.*, 1913, **2**, 98; *Chem. Abs.*, 1914, **8**, 1282; *J.S.C.I.*, 1913, **32**, 742B.

[8] *Canad. J. Research*, 1929, **1**, 240; *Chem. Abs.*, 1930, **24**, 53; *cf.* Canadian Patent 301,542, 1930; *Chem. Abs.*, 1930, **24**, 4127; Canadian Patent 306,629, 1930; *Chem. Abs.*, 1931, **25**, 715.

[9] U. S. Patent 220,397, Oct. 7, 1879.

[10] Curme, U. S. Patent 1,422,838, July 18, 1922; assigned to Carbide and Carbon Chemicals Corp.; *J.S.C.I.*, 1922, **41**, 686A.

[11] Austrian Patents 108,421, 1924, and 108,424, 1924; *Brit. Chem. Abs.* **B**, 1930, 50.

Other methods have been suggested for the photochemical chlorination of ethane, as for example the chlorination of paraffin hydrocarbons by exposure of the hydrocarbons and chlorine to actinic light or light from a mercury vapor lamp.[18] Tompkins[19] proposed the chlorination of ethane from coal gas by one of two methods; either the separation of ethane and methane by liquefaction followed by chlorination of the former in the presence of actinic light, or the chlorination of the gaseous mixture in the presence of actinic light of such intensity that the methane is not attacked. Snelling,[20] on the other hand, effected the photochemical chlorination of ethane by means of an illuminated cell with transparent baffles and gradually increasing the intensity of the actinic light. The products of the reaction are circulated in contact with a solvent for the halogenated hydrocarbons, such as oil or carbon tetrachloride.[20a]

Miscellaneous Processes. There are several other processes which are said to be applicable to the treatment of methane homologues generally. Those of Polanyi and von Bogdandy[21] and Payne and Montgomery[22] concern the chlorination of gaseous paraffin hydrocarbons, among which may be included ethane. In the former process the chlorination of paraffin hydrocarbons, such as methane or its immediate homologues or higher paraffins, is accomplished by treatment with chlorine in the gaseous phase in contact with catalysts such as an alkali metal or arsenic or phosphorus. The process of Payne and Montgomery contemplates the chlorination of gaseous paraffins (3 vols. of Cl_2 per vol. of hydrocarbon gas) in the gaseous phase at temperatures of about 300° F. in the presence of a special porous solid catalyst made by the complete chlorination of higher petroleum fractions, or of such oils mixed with powdered coal.[23] The chlorination of the gaseous paraffins may be completed after this catalytic treatment, if so desired, by a further treatment consisting of exposure to ultraviolet light in quartz tubes.

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[12] Kolbe and Frankland, *J.C.S.*, 1849, 1, 65.

[13] Frankland, *J.C.S.*, 1851, 3, 338.

[14] See footnote 12; the camphor-like substance may have been hexachloroethane.

[15] *J.C.S.*, 1864, 17, 262; *Proc. Roy. Soc.* (*London*), 1865, 14, 167.

[16] *Ann.*, 1869, 150, 217.

[17] *Abhandl. Krakauer. Akad. Wissensch.*, 1912, 52, 307; *Chem. Zentr.*, 1913, 2, 99; *Chem. Abs.*, 1914, 8, 1282.

[18] Graul and Hanschke, U. S. Patent 1,032,822, July 16, 1912; *Chem. Abs.*, 1912, 6, 2686; German Patent 261,677, 1911; *Chem. Abs.*, 1913, 7, 3641; British Patent 4766, 1912; *Chem. Abs.*, 1913, 7, 2854; all patents assigned to Badische Anilin- und Soda-Fabrik.

[19] British Patent 780, 1915; *J.S.C.I.*, 1915, 34, 1225.

[20] U. S. Patent 1,285,823, Nov. 26, 1918; *J.S.C.I.*, 1919, 38, 158A.

[20a] The use of ultraviolet radiation in the halogenation of paraffins was also discussed by Ellis and Wells, "The Chemical Action of Ultraviolet Rays," Chemical Catalog Co., Inc., New York, 1925, 195.

[21] British Patent 289,795, 1927; *Chem. Abs.*, 1929, 23, 847.

[22] Canadian Patent 268,301, 1927; *Chem. Abs.*, 1927, 21, 1660.

[23] See also Payne and Montgomery, U. S. Patent 1,453,766, May 1, 1923.

The preparation of liquid compositions which may be used as dry-cleaning agents and as solvents in the paint and varnish industry, by the chlorination of natural gases containing mainly methane, ethane, propane, and butane, has been described by Vivas.[23a] Natural gas, under a pressure of about 120 pounds per square inch, is passed into a closed container (lined with material resistant to hydrogen chloride) containing antimony or phosphorus pentachloride equivalent to 2 per cent of the weight of gas. Chlorine gas is then introduced at a rate gradually increasing from 2.5 per cent of the natural gas for the first hour to 10 per cent after the seventh hour until chlorination is complete. The hydrogen chloride is removed during the process and the temperature is maintained at about —15° to —20° C. by cooling. The resulting liquid is neutralized with dilute sodium hydroxide and is later separated.

Graul and Hanschke [24] proposed to effect the chlorination of ethane by exposing a gaseous mixture of this hydrocarbon and chlorine to the influence of a silent electric discharge.

Alkyl halides may be obtained by heating a liquid alkyl hydrogen sulphate or dialkyl sulphate in the liquid phase with aqueous hydrogen halides at 130° to 140° C. under pressure. From appropriate compounds, a 90 to 95 per cent yield of ethyl chloride or 1-chlorobutane is said to result.[25] Daudt [25a] proposed to make ethyl chloride by passing a mixture of ethyl ether with an excess of hydrogen chloride over alumina at about 360° C.

Ethyl chloride results from the reaction of gaseous hydrogen chloride and ethylene in the presence of catalysts [26]; it is also formed in 10 per cent yield by passing moist methyl chloride over finely divided platinum on asbestos at 275° C. and in a larger yield at 200° C. when passed over activated charcoal impregnated with bismuth chloride or zirconium chloride.[27] Ethyl chloride is used as a local anaesthetic and as a refrigerant. A non-inflammable refrigerant containing ethyl chloride and ethyl bromide, together with alcohol and diethyl carbonate, has also been suggested.[27a]

Attempts made to prepare pentachloroethane by chlorination of acetylene tetrachloride in the presence of catalysts in the liquid phase were unsuccessful, the products being always the hexachloroethane; pentachloroethane, however, is said to be obtainable by chlorination of the tetrachloro-compound under the influence of actinic light.[28]

The physical properties of the chlorinated derivatives have been tabulated in Chapter 20. From the viewpoint of its possible application for the synthesis of ethyl alcohol and its derivatives, chloroethane (ethyl chloride) is of interest.

Bromination of Ethane. Merz and Weith,[29] from their experiments on the bromination of ethyl iodide, predicted that the bromination of this hydrocarbon should yield tetrabromoethane and hexabromoethane.

[23a] U. S. Patent 1,920,282, Aug. 1, 1933; assigned to Safety Products, Inc.; *Chem. Abs.*, 1933, 27, 4939.

[24] *Loc. cit.*; see also German Patent 263,716, 1911; addition to 261,677; *Chem. Abs.*, 1914, 8, 211; British Patent 5125, 1912; *Chem. Abs.*, 1913, 7, 2854; both patents assigned to Badische Anilin- und Soda-Fabrik.

[25] I. G. Farbenindustrie A.-G., British Patent 370,211, 1931; *Brit. Chem. Abs.* **B**, 1932, 762.

[25a] U. S. Patent 1,920,846, Aug. 1, 1933; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1933, 27, 4818.

[26] See, for example, Suida, German Patent 369,702, 1921; assigned to Chem. Fabrik. vorm. Weiler-ter Meer; *J.S.C.I.*, 1923, 42, 578A.

[27] Farben. vorm. Meister, Lucius and Brüning, British Patent 196,272, 1923; *J.S.C.I.*, 1924, 43, 200B.

[27a] Sorensen, U. S. Patent 1,845,355, Feb. 16, 1932; *Chem. Abs.*, 1932, 26, 2257.

[28] Kokatnur, *J.A.C.S.*, 1919, 41, 120; *Chem. Soc. Abs.*, 1919, 116 (1), 145.

[29] *Ber.*, 1878, 11, 2235.

In an early process Mallet[30] reported the direct bromination of ethane by passage of a mixture of bromine and the hydrocarbon through charcoal or other porous material at 30° to 90° C.

PROPANE

Chlorination. The chlorination of propane has been very inadequately studied but it appears that this hydrocarbon is more easily chlorinated than methane and on chlorination readily yields monochlorides as well as highly chlorinated products. Chlorination may be effected thermally, or by the aid of catalysts or photochemically, the latter method having been investigated most thoroughly. The number of possible products is very great and a few of the lower chlorinated products are given in Table 119a. Only a relatively small number of the total possible chloro-derivatives have been definitely identified among the products of the chlorination of propane, most of the compounds in Table 118 having been prepared by indirect methods.

TABLE 119a.—*Lower Chloro-Derivatives of Propane.*

Systematic Name	Formula	B.P. ° C.	Density, d_0^t
1-Chloropropane (n-propyl chloride)	$CH_3CH_2CH_2Cl$	46.5°	0.9156 at 0° C. 0.8918 at 19.8° C.
2-Chloropropane (isopropyl chloride)	$CH_3CHClCH_3$	36.5°	0.8588 at 20° C.
1,2-Dichloropropane	$CH_3CHClCH_2Cl$	97.5°–98.5°	1.1656 at 14° C.
1,3-Dichloropropane	$CH_2ClCH_2CH_2Cl$	119°	1.201 at 15° C.
1,1-Dichloropropane	$CH_3CH_2CHCl_2$	85°–87°	1.143 at 10° C.
2,2-Dichloropropane	$CH_3CCl_2CH_3$	69.7°	1.827 at 16° C. (?)
1,1,2-Trichloropropane	$CH_3CHClCHCl_2$	140°	1.402 at 0° C.
1,1,3-Trichloropropane	$CH_2ClCH_2CHCl_2$	146°–148°	1.362 at 15° C.
1,2,3-Trichloropropane	$CH_2ClCHClCH_2Cl$	158°	1.417 at 15° C.

The purely thermal chlorination of propane, using an excess of hydrocarbon over chlorine and high temperatures and high space velocities, has been examined by Mason and Wheeler.[31] Under these conditions chlorination may be restricted to the production of the monochloro-compounds mainly. Both normal and iso-monochloro-compounds were formed, but the former always predominated. The experimental results of Mason and Wheeler are given in Table 120.

TABLE 120.—*Chlorination of Propane.*
(Empty reaction tube 1 cm. bore x 15 cm. long.)

	Expt. 1	Expt. 2
Temperature	700° C.	700° C.
Space velocity (reciprocal minutes)	960	795
Ratio $Cl_2:C_3H_8$	1:6.2	1:5
% Cl_2 in washers (as Cl_2)	Trace	Nil
% Cl_2 in washers (as HCl)	55.9	60.4
Cl_2 balance (% on input)		
As C_3H_7Cl	28.3	28.4
As $C_3H_6Cl_2$	—	2.3
In washers	55.9	60.4
Total	84.2	91.1
Yield of C_3H_7Cl (calculated on 100% Cl_2 balance)	88.2	74.6

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[30] U. S. Patent 220,397, Oct. 7, 1879.
[31] *J.C.S.*, 1931, 2282.

The experimental results are in good agreement with the theoretical formula of Martin and Fuchs for a bimolecular stage process.

No work on the catalytic chlorination of propane has been reported but Herzfelder [32] studied the chlorination of seven di- and tri-chloropropanes by means of antimony pentachloride at varying temperatures up to 190° C. The main products obtained by this worker are given in Table 120a:

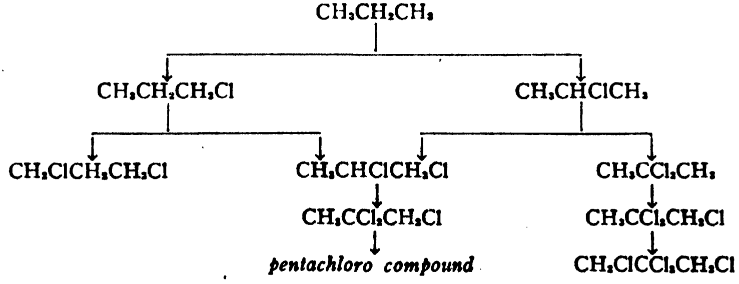
TABLE 120a.—*Products from Catalytic Chlorination of Di- and Tri-chloropropanes.*

Initial Material	Main Product
1,1-Dichloro-	1,1,2-Trichloro-
1,2-Dichloro-	1,1,2-Trichloro-
1,3-Dichloro-	1,1,3-Trichloro-
2,2-Dichloro-	1,2,2-Trichloro-
1,2,3-Trichloro	1,1,2,3-Tetrachloro-
1,2,2-Trichloro-	1,2,2,3-Tetrachloro-
1,1,2-Trichloro-	Pentachloro-

Mixtures of propane and chlorine appear to be stable in the dark but reaction takes place under the influence of sunlight, with the production of a complex mixture of chloro-substitution products. The reaction has been carefully investigated by Schorlemmer,[33] who found that exposure of equimolecular proportions of chlorine and propane to the influence of diffused sunlight led to the production of 1,2-dichloropropane, small quantities of n-propyl chloride, together with a mixture of more highly chlorinated products boiling between 100° and 200° C. Further exposure of a fraction boiling above 80° C. to the action of chlorine in direct sunlight led to the formation of trichloropropanes and a solid tetrachloropropane. A higher fraction boiling between 205° and 250° C. was acted on only very slightly by chlorine even in the presence of bright sunlight and complete chlorination to an octachloro-compound was not accomplished, though a liquid hexachloro-propane was isolated from the mixture.

The chlorination of isopropyl chloride in sunlight was found by Friedel and Silva [34] to furnish a mixture of 2,2-dichloro- and 1,2-dichloropropanes, the former being the preponderating product. However, by heating isopropyl chloride with pure iodine monochloride to 120° C. only 1,2-dichloropropane was formed and no 2,2-dichloropropane.

On the basis of the very inadequate state of our knowledge, the first few stages of the progressive chlorination of propane may perhaps be represented by the following scheme:



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[32] *Ber.*, 1893, **26**, 2432; *Chem. Soc. Abs.*, 1894, **66**, (1), 1.

[33] *Proc. Roy. Soc. (London)*, 1868, **16**, 35; *Ann.*, 1869, **150**, 210; *Ann. chim. phys.*, 1870, (4), **19**, 439.

[34] *Z. für Chem.*, 1872, (2), **7**, 489.

The industrial methods relating specifically to the chlorination of propane are very few. Snelling[35] stated that his process of photochemical chlorination, in which the reacting gases are illuminated by light of gradually increasing intensity is applicable to propane and other paraffin hydrocarbons. The halogenation of propane and butane to yield monohalogen derivatives is accomplished by the Bataafsche Petroleum Maatschappij[36] by mixing that hydrocarbon with chlorine gas in the dark and then exposing to a temperature of 330° to 380° C. without access of light. All the halogen is said to be used up and no carbonization or flame production takes place. According to one process developed by the Union Carbide Co., dichloropropane may be obtained relatively free from higher chlorinated products by the treatment of an excess of liquid propane with liquefied chlorine, while an inert solvent (e.g., carbon tetrachloride or some preformed dichloropropane) may be used to control the reaction.[37] Use of an excess of chlorine or of propane in the gaseous condition is said to result in the formation of some trichloro-compounds.

With the exception of the two monochloro-derivatives (n- and iso-propyl chlorides) and of 1,2-dichloropropane (propylene dichloride) the chlorinated propanes are almost unknown except as laboratory preparations. The monochloro-derivatives might be utilized in the manufacture of the respective alcohols if their economical production in a relatively pure condition, i.e., free from higher chlorinated products, could be effected.

Bromination. By the action of bromine on propane in the presence of iron as a catalyst, Mereshkowsky[38] reported the formation of tetra-, penta-, and hexa-bromo-derivatives, but experimental details are not definite. A pentabromo-derivative of propane was obtained by Merz and Weith[39] by the action of bromine on allyl bromide at 210° C. in the presence of iodine.

The bromination of propane at elevated temperatures is described by Snelling,[40] who proposes to circulate the gas mixture after reaction in contact with an inert solvent to remove halogenated products.

NORMAL BUTANE

Chlorination. Like its lower homologues, n-butane does not appear to react directly with chlorine in the dark at ordinary temperatures but reaction immediately occurs under the influence of diffused daylight. As might be expected the reaction product is usually a mixture in which mono- and di-chloro-derivatives have been definitely found. As early as 1849, Frankland observed the reaction of dry chlorine with dry butane on exposure of diffused daylight. Schöyen[41] exposed a mixture of butane and chlorine (over water) to diffused sunlight and noted the formation of hydrochloric acid and of a liquid insoluble in water. This latter product consisted of a mixture of butyl chloride, butylene chloride, and more highly chlorinated products. The production of a butyl chloride when butane from American petroleum was allowed to react with two volumes of chlorine in the presence of light was reported by Ronalds.[42] On the other hand, by exposure of a mixture of ten volumes of butane and nine volumes of chlorine to daylight, Butlerov[43] obtained a liquid product containing more chlorine than a dichlorobutane.

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[35] U. S. Patents 1,271,790, July 9, 1918; 1,285,823, Nov. 26, 1918; 1,421,733, July 4, 1922.

[36] British Patent 338,742, 1929; *Brit. Chem. Abs.* B, 1931, 237.

[37] British Patent 137,247, 1919; *J.S.C.I.*, 1920, **39**, 174A.

[38] *Bull. soc. chim.*, 1925, (4), **37**, 864; *Chem. Abs.*, 1926, **20**, 38.

[39] *Ber.*, 1878, 11, 2235.

[40] U. S. Patent 1,421,733, July 4, 1922; *Chem. Abs.*, 1922, **16**, 2867.

[41] *Ann.*, 1864, **130**, 233.

[42] *Trans. Roy. Soc. Edinburgh*, 1864, **23**, 496; *J.C.S.*, 1865, **18**, 60.

[43] *Ann.*, 1867, **144**, 15.

The work of Mabery and Hudson[44] was carried out on a fraction of Pennsylvania and Ohio naphtha of boiling point —2° to +2° C. This was chlorinated in the cold in the presence of diffused light in order to obtain smooth chlorination and the maximum production of monochlorinated products. The main portion of the monochloro-compound fraction boiled, however, at 68° to 69° C. and was thought to be isobutyl chloride. In no case was n-butyl chloride found. Similarly Pelouze and Cahours[45] chlorinated a petroleum distillate of boiling point 5° to 10° C. in diffused light and obtained a product boiling between 65° and 70° C. possessing the properties and composition of a butyl chloride. This could hardly have been n-butyl chloride, which boils at 78.5° C. at 760 mm.[46]

n-Butane can give rise to two isomeric butyl chlorides of the formulas $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$ respectively while there are six possible dichloro-derivatives. In the present inadequate state of our knowledge of the chlorination of n-butane it is impossible to assign definite formulas to the products observed.

Most processes which deal with the chlorination of higher hydrocarbons do not mention specifically the conditions necessary for butane alone but refer more generally to the chlorination of its immediate higher homologues, particularly pentane. The main accelerating agency mentioned is sunlight or actinic light but later work favors purely thermal chlorination in the absence of light, since it is claimed that by the latter method the chlorination reaction may be restricted to the formation of monochlorinated products.

Graul and Hanschke[47] suggested the vapor-phase chlorination of low-boiling paraffins in the presence of light from a mercury-vapor lamp. An excess of hydrocarbon vapor is used and the temperature is maintained at a point sufficient to maintain the hydrocarbon wholly in the vapor phase (reduced pressure may be employed). Snelling[48] proposed to convert butane mainly into butyl chloride by mixing chlorine with an excess of hydrocarbon vapor in a reaction vessel from which the gaseous mixture can be circulated and brought into contact with a solvent for the halogenated products (suitable solvent is carbon tetrachloride) and then a second solvent to remove hydrogen chloride. The photochemical chlorination of butane and other paraffins to butyl and alkyl chlorides can be carried out, according to Brooks, Essex and Smith,[49] in such a way that the mixture of gaseous or liquid reactants approaches the source of illumination in a gradual manner. The thermal chlorination of butane to form monochlorobutane (and also of other paraffins of more than two carbon atoms to furnish monochloro-derivatives generally) is accomplished by Ayres[50] by mixing the hydrocarbon vapor with a smaller volume of chlorine and heating (in the absence of actinic light, electric discharge, or catalyst) to a temperature sufficient to produce a preponderance of monochlorinated products and simultaneously to effect a complete consumption of the chlorine. Another proposal[51] was for the monochlorination of propane or butane in the vapor phase and in the dark at 330° to 380° C. and also presumably in the absence of catalysts. The main product is stated to be the alkyl halide and the reaction is said to be effected smoothly with complete utilization of the chlorine (or bromine) present in the reacting gases.

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[44] *Proc. Amer. Acad. Arts. Sci.*, 1897, **32**, 101; *Amer. Chem. J.*, 1897, **19**, 243.

[45] *Compt. rend.*, 1862, **54**, 1241; 1863, **56**, 505; **57**, 62.

[46] Timmermans and Hennault-Roland, *J. chim. phys.*, 1930, **27**, 401; *Chem. Abs.*, 1931, **25**, 2038.

[47] U. S. Patent 1,032,822, July 16, 1912; *Chem. Abs.*, 1912, **6**, 2686; British Patent 4766, 1912; *Chem. Abs.*, 1913, **7**, 2854; German Patent 261,677, 1911; *Chem. Abs.*, 1913, **7**, 3641; all patents assigned to Badische Anilin- und Soda-Fabrik.

[48] U. S. Patent 1,421,733, July 4, 1922; *Chem. Abs.*, 1922, **16**, 2867.

[49] U. S. Patent 1,191,916, July 18, 1916; *Chem. Abs.*, 1916, **10**, 2297.

[50] U. S. Patent 1,741,393, Dec. 31, 1929; *Chem. Abs.*, 1930, **24**, 1119.

[51] Bataafsche Petroleum Maatschappij, British Patent 338,742, 1929; *Brit. Chem. Abs.* **B**, 1931, 237. For the description of an apparatus for such chlorination processes see Bataafsche Petroleum Maatschappij, French Patent 715,187, 1931; *Chem. Abs.*, 1932, **26**, 1479.

It has been stated that the presence of small proportions of unsaturated hydrocarbons facilitates the halogenation of saturated hydrocarbons, that is, halogenation by substitution is improved by conducting it simultaneously with an addition reaction.[51a] For example, a reaction between butane and chlorine carried out in the dark is accelerated by the presence of about 10 per cent of butylene. However, if air or oxygen is introduced into a mixture of saturated and unsaturated hydrocarbons, the substitution is apparently suppressed and the addition proceeds. Thus, in the above reaction most of the butane remains unchanged, dichlorobutane being mainly formed.[51b]

Bromination. As in the case of the chlorination of n-butane the bromination of this hydrocarbon has been very inadequately studied. Frankland[52] observed that bromination occurred under the influence of direct sunlight or at slightly elevated temperatures, and Carius and Lisenko[53] obtained a colorless liquid boiling between 155° to 162° C. (without decomposition), and having bromine content corresponding to that of butylene bromide ($C_4H_8Br_2$), by heating bromine and butane together for several hours in a sealed tube at 100° C. Butlerov[54] obtained a heavy oil, consisting mainly of polybrominated products, by the influence of daylight on an equimolecular mixture of butane and bromine.

Jacobson[54a] prepared 1,2,3,4-tetrabromobutane by passing 2,3-dibromobutane or crotyl chloride (4-chloro-2-butene) over soda-lime at 400° to 550° C. and subsequently absorbing the gaseous product in bromine. The compound, purified by two crystallizations from alcohol, melted at 116° to 117° C., the yields being about 13 to 20 per cent. The condensate which came over after the excess bromine was distilled off consisted of 2,3-dibromobutane (boiling point, 157.5° to 159° C.) and trans-2-bromo-2-butene (boiling point, 90.5° to 92.5° C.). The by-products found in the liquid residues were 1,2-dibromobutane (boiling point, 165° to 166° C.), 2,3-dibromobutane (boiling point, 158° to 159° C.), 1,3-dibromobutane (boiling point, 173° to 175° C.), 1,4-dibromobutane (boiling point, 197° to 198° C.), 1,1,4,4-tetrabromobutane (boiling point, 133° C. at 1 mm.), and isomeric 1,2,3,4-tetrabromobutane (melting point, 38° C.).

ISOBUTANE

Most of the work on this hydrocarbon has been carried out on petroleum fractions containing isobutane mixed with other homologous paraffins and also probably with some n-butane.

As previously mentioned Mabery and Hudson[55] found that chlorination of a petroleum fraction, boiling point —2° C. to +2° C., in the cold and in the presence of diffused sunlight resulted principally in monochlorination. On fractionation of the products about 80 per cent boiled at 68° to 69° C., and this portion was thought to be isobutyl chloride. A dichlorobutane, boiling point 121° to 122° C., was obtained also after prolonged fractional distillation. Similarly Aschan[56] chlorinated a petroleum fraction of boiling point 10° to 12° C. in the presence of water and obtained, as the main product, a monochloride with a

[51a] Bataafsche Petroleum Maatschappij, French Patent 745,543, 1933; *Chem. Abs.*, 1933, 27, 4240.

[51b] Bataafsche Petroleum Maatschappij, French Patent 745,544, 1933; *Chem. Abs.*, 1933, 27, 4240.

[52] *Ann.*, 1849, 71, 202, 205.

[53] *Ann.*, 1863, 126, 214.

[54] *Ann.*, 1867, 144, 15; *Z. für Chem.*, 1867, 10, 363.

[54a] *J.A.C.S.*, 1932, 54, 1545.

[55] *Loc. cit.*

[56] *Översikt Finska Vetenskaps-Soc. Förh.*, 1915, 58, 122; *Chem. Abs.*, 1920, 14, 3654.

boiling range of 60° to 70° C., and which was considered to be derived from the isobutane present in the petroleum fraction.

Later work on the chlorination of the butanes by Hass and McBee[57] indicated that the monochloride isolated by Mabery and Hudson was 2-chlorobutane, rather than isobutyl chloride, and also that the dichloride isolated by these same workers was probably either 1,2- or 2,3-dichlorobutane. Possibly the monochloride isolated by Aschan consisted largely of 2-chlorobutane rather than isobutyl chloride.

On the other hand, Butlerov[58] studied the photochemical reaction of ten volumes of isobutane and nine volumes of chlorine and obtained tertiary butyl chloride, together with a higher-boiling mixture of products of slightly higher chlorine content than indicated by the formula $C_4H_8Cl_2$.

Heating isobutane with iodine monochloride[59] at 250° C. caused disruption of the molecule with the production of hexachloroethane and carbon tetrachloride.

Bromination. Only polybrominated products were obtained by Butlerov[60] by the reaction of equimolecular proportions of isobutane and bromine. The bromination, however, occurred more readily in this case than in the case of n-butane. The bromination of isobutane in the presence of iron as a catalyst was found by Mereshkovski[61] to give rise to tetra-, penta-, and hexa-brominated products. By the action of bromine on isobutyl bromide at 175° C. a hexabromoisobutane is produced, while at 300° to 340° C. hexabromoisobutylene was found among the products of reaction.[62]

NORMAL PENTANE

Chlorination. The action of chlorine in diffused daylight at ordinary temperature on a hydrocarbon fraction (boiling point 32° to 35° C.), obtained by the distillation of crude fatty acids with superheated steam was found by Cahours and Demarcay[63] to result in the production of a liquid boiling at about 100° C. and having the properties of an amyl chloride. Similarly Schorlemmer[64] obtained, by the vapor phase chlorination of a petroleum fraction boiling at 37° to 39° C., a mixture of amyl chlorides of boiling range 95° to 110° C., the main fraction distilling at 100° to 102° C.

Rather more definite information regarding the chlorination of pure n-pentane to amyl chlorides is furnished by the work of Lachowicz[65] and Aschan.[66] The former worker passed a slow stream of chlorine into the vapors of n-pentane at room temperature, the reaction being afterwards accelerated by heating at water-bath temperature. Two amyl chlorides were formed, one boiling at 106° C. (1-chloropentane?) being present in larger amount, and the other, possibly a secondary chloride, boiling at 104° C. Aschan found that the best results were obtained by using dry gaseous mixtures and definitely identified 1-chloropentane (boiling point 107° C.) among the products as well as a secondary amyl chloride (boiling point 96° to 98° C.). Bauer[67] passed chlorine into liquid pentane for several hours and obtained a product boiling at 230° to 240° C. and of a composition corresponding approximately with the formula $C_5H_8Cl_4$.

In connection with the chlorination of pentane as reported by Aschan it has been pointed out by Hass and Weber (unpublished) that 1-chloropentane boils about 10° C. higher than either 2-chloro- or 3-chloropentane, and that the two latter chloro derivatives boil within about 0.3° C. of each other. Separation of 2- and 3-chloropentane by distillation can hardly be expected, and this probably explains why Aschan reported only one secondary amyl chloride instead of two.

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[57] Private communication from Professor H. B. Hass of Purdue University.

[58] *Ann.*, 1867, **144**, 15.

[59] Krafft and Merz, *Ber.*, 1875, **8**, 1296.

[60] *Ann.*, 1867, **144**, 15; *Z. für Chem.*, 1867, **10**, 363.

[61] *Bull. soc. chim.*, 1925, **37** (4), 864; *Chem. Soc. Abs.*, 1925, **128** (1), 1033.

[62] Merz and Weith, *Ber.*, 1878, **11**, 2235.

[63] *Compt. rend.*, 1875, **80**, 1568.

[64] *Phil. Trans.*, 1872, **162**, 114; *Ann.*, 1872, **161**, 268.

[65] *Ann.*, 1883, **220**, 173.

[66] *Oversikt Finska Vetenskaps-Soc. Förh.*, 1915, **58**, 122; *Chem. Abs.*, 1920, **14**, 3654.

[67] *Compt. rend.*, 1860, **51**, 572.

Ayres[68] and Clark[69] have reported the results of the large-scale chlorination of n- and isopentane by the Sharples Solvents Corporation. A fuller description of the technical development of this process is given in a later section of this chapter.

Chlorination of the two pentanes at temperatures below 100° C. in either vapor or liquid phase was found to need the accelerating influence of light or catalysts. In the presence of the latter, however, the chlorination tends to proceed beyond the monochloro stage and the yields of primary chlorides are low. On the other hand, chlorination above 200° C. in the vapor phase (liquid phase requires inconveniently high pressures) can be accomplished without the aid of catalysts and results in the highest yields of primary chlorides. The presence of anhydrous polyvalent metallic chlorides reduces the yield of primary chlorides while carbon or pumice have little influence either on yield of primary chloride or on reaction velocity. Catalysts, such as iodine, sulphur chloride, or red phosphorus, which are volatile and soluble in liquid pentane, cause the excessive production of polychloro-derivatives. The use of insoluble and non-volatile catalytic metallic chlorides results in the production of high yields of monochlorides in either liquid or vapor phase operation but unfortunately causes the isomerization of the primary chlorides to secondary and tertiary chlorides which are of less industrial value in alcohol manufacture. Particularly at higher temperature, such catalysts appear also to accelerate the formation of amylenes and the polymerization of these amylenes. This effect has been frequently noted in the case of the propyl and butyl chlorides.[70]

In the case of n-pentane all three possible monochloro-compounds, namely, 1-chloro-, 2-chloro- and 3-chloropentanes, are formed but in the presence of catalysts or under the prolonged influence of heat and pressure, both the 1-chloro- and the 2-chloro-derivatives are isomerized to the 3-chloro-derivative. This isomerization process undoubtedly proceeds by splitting off and subsequent addition of the elements of hydrogen chloride with the intermediate production of amylenes, thus:

$$\begin{array}{c}
CH_3CH_2CH_2CH_2CH_2Cl \\
\downarrow \\
CH_3CH_2CH_2CH{=}CH_2 + HCl \\
\downarrow \\
CH_3CH_2CH_2CHClCH_3 \\
\downarrow \\
CH_3CH_2CH{=}CHCH_3 + HCl \\
\downarrow \\
CH_3CH_2CHClCH_2CH_3
\end{array}$$

Only the last of these reactions is a reversible process.

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[68] *Ind. Eng. Chem.*, 1929, 21, 899.

[69] *Ind. Eng. Chem.*, 1930, 22, 439.

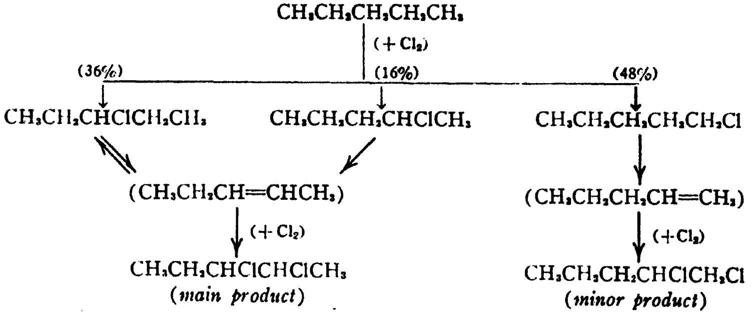
[70] Brunel, *Ber.*, 1911, 44, 1000; Eltekov, *Ber.*, 1875, 8, 1244; Favorsky, *Ann.*, 1907, 354, 325; Gustavson, *J. Russ. Phys.-Chem. Soc.*, 1883, 15, 61; Kekulé and Schrötter, *Ber.*, 1879, 12, 2279; Michael, Scharf and Voigt, *J.A.C.S.*, 1916, 38, 653; Mouneyrat, *Bull. soc. chim.*, 1899, 21 (3), 616.

The optimum conditions for the formation of primary monochlorides from pentanes with minimum production of secondary and tertiary monochlorides or of higher chloro-compounds, amylenes, or polymerized amylenes were found to be: Rapid passage of a gaseous mixture of chlorine and excess of pentanes through a hot reaction zone (at 315° to 371° C.) at such a rate that the period of reaction is shortened to about 2.5 seconds. Under these conditions, n-pentane yields the following proportions of isomeric monochlorides:

1-Chloropentane, boiling point 107° C., approximately 48%
2-Chloropentane, boiling point 97° C., approximately 16%
3-Chloropentane, boiling point 96° C., approximately 36%

Besides the above monochlorides a number of dichloro-compounds are formed simultaneously though in small yields. Almost none of the dichlorides formed by progressive chlorination of pentane, such as the 1,1- or 1,5-compounds, was found among the dichloro-products of this vapor phase thermal chlorination. 1,2-Dichloropentane was present in minor proportions while 2,3-dichloropentane was the major constituent. The formation of these products may be summarized as follows:

Vapor Phase Thermal Chlorination of N-Pentane.



Bromination. By exposing a mixture of a fraction of Rumanian petroleum (boiling at 0° to 10° C.) and bromine in the presence of water to diffused sunlight for 4 to 14 days, Poni[71] obtained a number of bromopentanes which were all derivatives of isopentane and tetramethylmethane.

Dow[72] has suggested the bromination of pentane in the presence of an iron catalyst to separate that hydrocarbon from carbon disulphide. Both the pentane and the carbon disulphide are among the recovered volatile products from the distillation of coal.

ISOPENTANE

Chlorination. The work on this hydrocarbon has been carried out using fractions of narrow boiling range and containing quantities of other hydrocarbons. Pelouze and Cahours[73] noted that a petroleum fraction of boiling point 30° to 32° C. absorbed chlorine rapidly in diffused daylight even at ordinary temperature. By stopping the reaction while some hydrocarbon was still unchlorinated, and thus avoiding an excess of chlorine, an amyl chloride mixture of boiling point

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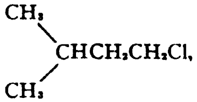
[71] *Ann. sci. univ. Jassy*, 1905, **3**, 212; *Chem. Soc. Abs.*, 1906 **90** (1), 1; *Chem. Zentr.*, 1906, **1**, 442.
[72] U. S. Patent 1,317,359, Sept. 30, 1919; *Chem. Abs.*, 1919, **13**, 3310.
[73] *Compt. rend.*, 1862, **54**, 1241; 1863, **56**, 505; **57**, 62.

98° to 103° C. was obtained. Monochloroisopentanes boiling at 99.8° to 100.5° C. (probably mainly primary isoamyl chloride) were obtained by Lachowicz[74] by chlorination of a fraction (boiling point 29° to 30° C.) of Galician petroleum. Mabery and Hudson[75] subjected a distillate of the same boiling range, from Pennsylvania and Ohio petroleums, to chlorination in the presence of diffused daylight at ordinary temperatures and obtained a chlorinated product about 85 per cent of which boiled at 96.5° C. This proved to be isoamyl chloride. Another constant boiling product, boiling point 144° to 145° C., was obtained after eighteen distillations and possessed the composition of a dichloropentane. According to Mott and Bedford,[76] the photochemical chlorination of isopentane at room temperature takes place twice as rapidly under the influence of a white flame arc as when exposed to a quartz mercury-vapor lamp. The active rays from the white flame arc were thought to be concentrated in the blue region of the visible spectrum.

One of the most comprehensive investigations of the chlorination of isopentane from petroleum is that of Aschan.[77] Dry chlorination of isopentane was found to yield a mixture of the four isopentyl chlorides:

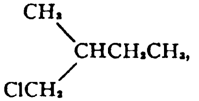
4-Chloro-2-methylbutane,



$$(CH_3)_2CHCH_2CH_2Cl$$

boiling point 99°–102° C., d_{15}^{15} 0.8692.

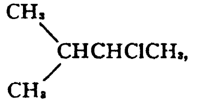
1-Chloro-2-methylbutane,



$$\begin{matrix}CH_3\\ClCH_2\end{matrix}\!\!>CHCH_2CH_3$$

boiling point 96°–99° C., d_{15}^{15} 0.8818.

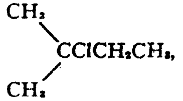
3-Chloro-2-methylbutane,



$$(CH_3)_2CHCHClCH_3$$

boiling point 90°–93° C., d_{15}^{15} 0.8752.

2-Chloro-2-methylbutane,



$$(CH_3)_2CClCH_2CH_3$$

boiling point 85.5°–88° C., d_{15}^{15} 0.8692.

Some dichlorides were also obtained.

On the other hand, chlorination of isopentane in the presence of water vapor led to the production of large proportions of *secondary* chloride but no *tertiary* isoamyl chloride.

By the purely thermal vapor phase chlorination process described by Ayres[78] for the production of maximum yields of primary monochlorides, isopentane is said to yield three monochlorides, of which two primary are present together with some tertiary but, in contradistinction to the results of Aschan, no secondary chloride.[79] The boiling points and proportions of the products are as follows:[80]

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[74] *Ann.*, 1883, **220**, 173.

[75] *Proc. Amer. Acad. Arts Sci.*, 1897, **32**, 101; *Amer. Chem. J.*, 1897, **19**, 243.

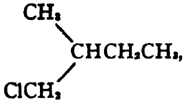
[76] *J. Ind. Eng. Chem.*, 1916, **8**, 1033.

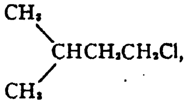
[77] *Översikt Finska Vetenskap-Soc. Förh*, 1915, **58**, 122; *Chem. Abs.*, 1920, **14**, 3654.

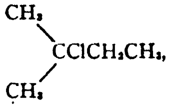
[78] *Ind. Eng. Chem.*, 1929, **21**, 899.

[79] The failure to obtain a secondary chloride in the process described by Ayres may be due to the relatively long periods of heating and digestion which cause it to disappear (Hass, private communication).

[80] Clark, *Ind. Eng. Chem.*, 1930, **22**, 439.

1-Chloro-2-methylbutane,  boiling point 99° C., 60 per cent.

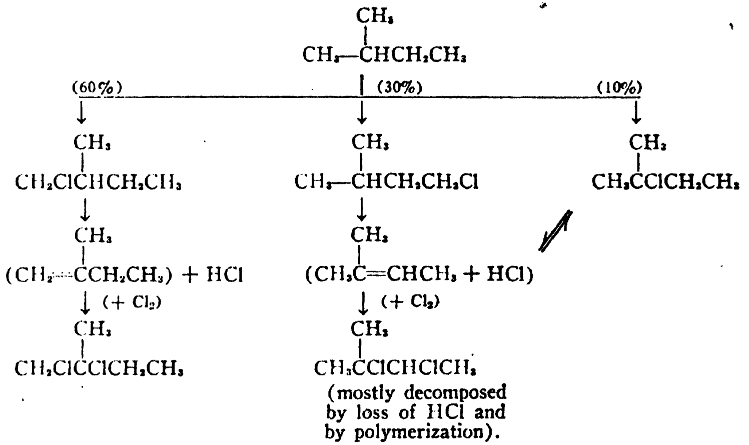
4-Chloro-2-methylbutane,  boiling point 101° C., 30 per cent.

2-Chloro-2-methylbutane,  boiling point 86° C., 10 per cent.

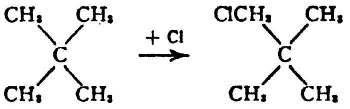
Besides monochlorinated products, this method of chlorination also yields quantities of isoamylenes and dichloroisopentanes. The latter substances are all dichloro-compounds evidently derived from isoamylenes produced by the splitting off of hydrogen chloride from the monochlorides. The dichloride of isopropylethylene (3,4-dichloro-2-methylbutane) does not occur, but 2,3-dichloro-2-methylbutane and 1,2-dichloro-2-methylbutane are present, though the first of these two is mostly destroyed by polymerization.

The chlorination of isopentane in the vapor phase at high temperatures using an excess of hydrocarbon over chlorine may be briefly summarized as follows:

Thermal Chlorination of Isopentane.



Chlorination of Tetramethylmethane. By allowing a mixture of this hydrocarbon and chlorine to remain in contact at room temperature in the presence of ordinary light, Tissier[81] obtained the only possible monochloro-derivative:



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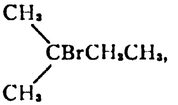
[81] *Ann. chim. phys.*, 1893, 29 (6), 344; *Chem. Soc. Abs.*, 1893, 64 (1), 542.

This monochloro-compound has been prepared in considerable quantities by the thermal vapor phase chlorination method just described.

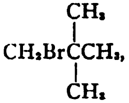
Bromination of Isopentane and Tetramethylmethane. By the bromination of a fraction, boiling point 0° to 10° C., of Colibasi petroleum in diffused sunlight in the presence of water vapor, Poni[82] obtained a number of bromo-compounds derived from isopentane and tetramethylmethane, and to these products the following formulas were assigned:

2-bromo-2-methylbutane



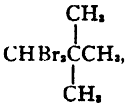
boiling point 108° to 109° C. at 745 mm.

1-bromo-2,2-dimethylpropane,



$CH_2Br\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3$, boiling point 89° to 91° C. at 749 mm.

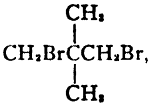
1,1-dibromo-2,2-dimethylpropane,



$CHBr_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3$, boiling point 64° to 65° C. at 43 mm.

and

1,3-dibromo-2,2-dimethylpropane,



$CH_2Br\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2Br$, boiling point 82° to 83° C. at 49 mm.

CHLORINATION OF MIXED PENTANES

Since the industrial separation of individual pentanes in a pure condition from petroleum fractions is a tedious process, a considerable amount of research has been directed toward the chlorination of a mixture of isomeric pentanes largely with a view to the commercial production of mixtures of amyl alcohols. The results of these efforts are embodied in a number of processes which are discussed later. Interesting details of the photochemical chlorination of a pentane fraction, boiling point 24° to 25° C., have been supplied by Brooks, Smith and Essex.[83] Chlorination in the vapor phase in diffused sunlight gave the best yields of amyl chlorides when a large excess of hydrocarbon was present, i.e., 2 to 4 times as much as that theoretically required. When employing 3 moles of hydrocarbon to 1 mole of chlorine, 88 per cent of the chlorinated products were monochloroderivatives. When chlorinating in the liquid phase, under the influence of illumination and at temperatures below 10° C., 90 to 94 per cent of the chlorinated products consisted of monochloro-derivatives, and the chlorination was stopped before the concentration of chlorine derivatives in the liquid exceeded about 20 per cent of the mixture. From the chlorinated products a monochloropentane fraction suitable for conversion into amyl acetate was obtained. Although illumination of the liquid reaction mixture was not absolutely necessary for reaction the process was usually initiated by exposure to light from a high-power tungsten bulb in the upper part of the reaction chamber. The presence of moisture appeared to aid the chlorination.

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[82] *Ann. Sci. Univ. Jassy*, 1905, 3, 212; *Chem. Zentr.*, 1906, 1, 442.
[83] *J. Ind. Eng. Chem.*, 1918, 10, 511.

Garner[84] described a method in which natural-gas gasoline boiling between 40° and 70° C. was chlorinated in the presence of ultraviolet light to furnish amyl chloride. Later Dobryanski and Gurevich[85] investigated the chlorination of the pentane fraction (boiling point 31° to 38° C.) of Krasnodar aviation gasoline in artificial light. For the maximum production of monochloro-products, chlorination by means of dry chlorine in the vapor phase at 60° to 70° C. was found to be most suitable.

INDUSTRIAL APPLICATION OF THE CHLORINATION OF THE PENTANES

The chlorination of the pentanes for the production of monochloro-derivatives capable of being converted into various amyl alcohols or their esters has received much attention as a possible method for the large scale manufacture of these important solvents. While the development of such chlorination processes has taken place largely in the United States there has been considerable interest abroad in the possibilities of this type of synthesis. In many cases the method proposed is claimed to be applicable not only to mixtures of pentane and isopentane but also to hexanes, heptanes, and octanes. For convenience these are discussed at this point rather than under each individual higher homologue.

Photochemical Chlorination. The light fraction (b.p., 28° to 69° C.) of gasoline, consisting principally of pentane, isopentanes, hexanes, and isohexanes, can be chlorinated in the presence of light to yield principally mono- and dichloro-compounds.[86] These compounds may then be treated with sodium acetate and acetic acid to yield the corresponding acetates, which are solvents for cellulose nitrate. In another process Sparre and Masland[87] first saturated the liquid hydrocarbon with chlorine in the dark and then exposed the mixture to daylight or to the light from a mercury vapor lamp. By carrying out the chlorination in tubes in absence of any appreciable quantity of the gas phase and by regulating the intensity of the light risk of explosion was greatly reduced.

According to Graul,[88] the vapors of a petroleum fraction consisting principally of n-pentane and isopentane and boiling between 40° and 45° C. are chlorinated by mixing with chlorine and then exposing the mixture to chemically active illumination. The monochloro products thus formed are next treated with calcium oxide at 375° to 450° C. to effect the elimination of hydrogen chloride and the formation of the olefin. The olefin is then allowed to react with hydrogen chloride to obtain 2-chloroisopentane.

The photochemical chlorination of liquid saturated hydrocarbons was carried out by Brooks, Essex and Smith.[89] The liquid hydrocarbons are introduced into a container made of some suitable chlorine-resisting material and provided with a pair of windows through which the color of the liquid may be observed. Inside the container is placed a coil, through which either a cooling or heating medium may be circulated. Near the top of this container is suspended a lamp which is the source of irradiation, while at the bottom is a perforated pipe through which the chlorine is fed. A stirrer is also provided so as to keep the hydrocarbons well agitated while chlorine is being introduced. Furthermore the container is connected to a series of condensers and receivers for collecting any volatile products which may be formed. The intensity of illumination from the lamp is diminished as it travels downward through the liquid while the concentration of chlorine diminishes steadily from the bottom of the liquid upwards. This results in the illumination being the most intense in that portion of the liquid which contains the lower chlorine concentration. Therefore a smooth reaction is obtained which yields principally monochlorinated products. In addition, formation of di- and polychlorinated products is prevented by stopping chlorination as soon as about 20 per cent of the hydrocarbons have been converted to monochlorides.

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[84] *Nat. Gas and Gasoline J.*, 1918, **12**, 328; *Gas Age*, 1918, **41**, 559: *Amer. Gas. Engr. J.*, 1918, **108**, 491, 506; *Proc. Nat. Gas Assoc.*, 1918, **10**, 136.

[85] *Neft. Khoz.*, 1928, **15**, 532; *Brit. Chem. Abs.* **B**, 1930, 131.

[86] Sparre, U. S. Patent 1,148,258, July 27, 1915; *Chem. Abs.*, 1915, **9**, 2593; British Patent 29,963, 1912; *J.S.C.I.*, 1914, **33**, 502; both assigned to E. I. duPont de Nemours & Co., Inc.

[87] U. S. Patent 1,148,259, July 27, 1915; *Chem. Abs.*, 1915, **9**, 2612; U. S. Patent 1,379,367, May 24, 1921; *Chem. Abs.*, 1921, **15**, 3392; both assigned to E. I. duPont de Nemours & Co., Inc. Also French Patent 453,406, 1913; *J.S.C.I.*, 1913, **32**, 767.

[88] U. S. Patent 1,202,282 Oct. 24, 1916; assigned to Badische Anilin- und Soda-Fabrik; *Chem. Abs.*, 1917, **11**, 224.

[89] U. S. Patent 1,191,916, July 18, 1916; assigned to Gulf Refining Co.; *Chem. Abs.*, 1916, **10**, 2297.

The process of Graul and Hanschke[90] refers to the photochemical chlorination of saturated hydrocarbons (which are normally liquid) in the vapor phase under the influence of ultraviolet light. For example 1000 parts of a purified Galician petroleum fraction, of boiling point 88° to 92° C., consisting chiefly of isopentane, is placed in a lead-lined vessel provided with a fractionating column, and raised to the boiling point at an absolute pressure of 50 mm. The vapors are mixed with (700 parts) chlorine and the mixture then passed through a vessel containing a mercury vapor lamp where chlorination occurs. The chlorination product consists chiefly of a monochloro-isoheptane of boiling point about 140° C. By treatment of a Galician petroleum fraction of boiling point 75° to 81° C. in a similar manner there is obtained a product boiling at 135° to 145° C., the analysis of which agreed with that of a monochlorocyclohexane. The chlorination products are condensed together with unchanged hydrocarbon and returned to the vaporizer, while the vapors of hydrogen chloride pass on and are condensed.

In contrast to the two previous processes Boyd[91] proposed to employ a continuous two-phase process of photochemical chlorination.

According to Boyd, the use of a two stage process obviates the contamination of the resulting hydrochloric acid with unchanged chlorine, which is always obtained when employing a liquid phase process alone. Provided the production of monochloro-compounds is not allowed to exceed 25 per cent of the theoretical in either the liquid or gaseous phase reactors, the formation of polychloro-compounds is claimed to be held at a minimum. The apparatus consists of a series of reaction tubes, each of which is provided with transparent windows, one window at the top of the tube and the other at the bottom. The tubes are separated so as to allow a source of ultraviolet light to be placed between them: also a source of ultraviolet light above the uppermost tube and beneath the lowest tube. The liquid hydrocarbons are introduced into the system at the middle reaction tube and allowed to flow downwards through the reaction tubes countercurrent to the chlorine gas, which is introduced at the bottom of each reaction tube. From the bottom tube is withdrawn a mixture of unreacted hydrocarbons and chlorinated products. Any hydrocarbon gases pass upwards through this series of tubes, during which time they are continually mixed with chlorine and exposed to the action of ultraviolet light. From the top reaction tube the gaseous products are led through a condenser into a receiver and the liquid products so obtained added to those withdrawn from the bottom reaction tube. Any hydrogen chloride which has been formed during the process is collected at this point by passing the uncondensed gases through a scrubbing tank. The mixture of chlorinated products and hydrocarbons is pumped into a still which is heated to such a temperature as to effect distillation of the hydrocarbons but to leave the chlorinated products as a residue which is withdrawn.

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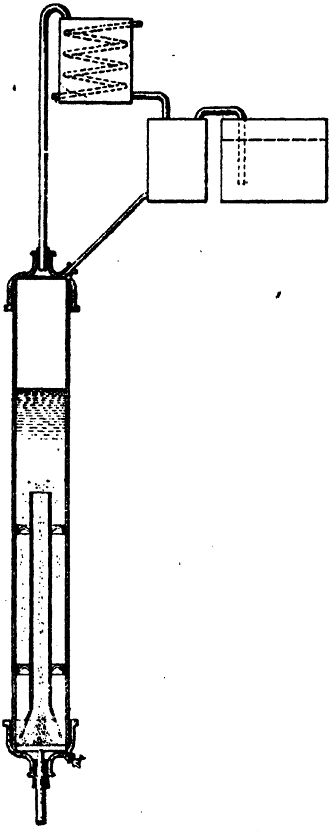
[90] U. S. Patent 1,032,822, July 16, 1912; assigned to Badische Anilin and Soda Fabrik; *Chem. Abs.*, 1912, 6, 2686.

[91] U. S. Patent 1,293,012, Feb. 4, 1919; assigned to Ohio Fuel Supply Co.; *Chem. Abs.*, 1919, 13, 1075.

The hydrocarbon vapors from the still are then passed through a condenser, and any liquid products are returned to the first system of reaction tubes, while the gaseous hydrocarbons are passed through a second series of reaction tubes in which they are mixed with chlorine, and again exposed to ultraviolet light. Separation of chlorinated products and hydrocarbons is again accomplished in exactly the same manner as described for the first series of reaction tubes and the hydrogen chloride formed is again separated by passing the uncondensed gases through a scrubbing tank.

Still another process for the chlorination of hydrocarbons is the one proposed by Lacy,[92] in which chlorine is dissolved in a liquid paraffin in contact with water, and the mixture subjected to the influence of chemically active light. The hydrogen chloride formed in this process is absorbed by the water layer.

Catalytic and Photochemical-Catalytic Processes. The photochemical-catalytic chlorination process developed by Koch and Stallkamp[93] and later described by Koch and Burrell[94] is applicable particularly to the conversion of pentane into amyl chlorides, which can then be hydrolyzed to alcohols. The apparatus, which is employed in this process (Fig. 29), consists of a lead-free glass tube fitted at the ends with reducers and screens. Inside this large tube is a smaller tube, also of lead-free glass, which extends approximately one-half of the vertical length of the large tube and is supported at a short distance above the bottom screen. A small nozzle projects through the bottom screen and this is directed into the lower end of the small tube. The lower end of the smaller tube is spread out in the shape of a funnel. Activated carbon, silica gel, or similar porous substances which possess large gas-absorption properties are used as catalyst or chlorine carriers. Activated carbon of 12- to 15-minute chloropicrin test was found to give the best results. The catalyst is placed on the bottom screen in the large tube to the depth of about 3 inches.



Courtesy Industrial and Engineering Chemistry

FIG. 29.—Apparatus for the Chlorination of Pentane. (Koch and Burrell.)

The large tube is filled about three-fourths full of pentane, and chlorine gas is forced into the apparatus through the small nozzle which is placed concentrically with respect to the funnel-shaped mouth of the smaller tube or percolator. The chlorine gas emerging from the nozzle passes up through the catalyst and then through the percolator tube, carrying some of the catalyst along with it. While flowing up through the percolator, the catalyzing material and chlorine are in intimate contact in the presence of a small quantity of the liquid, and large amounts of the chlorine are adsorbed by the catalyst. The catalyst passes out through the top of the percolator and enters the reaction zone, which is exposed to actinic light emanating from a battery of mercury vapor lamps. At this point it comes in contact with a large quantity of pentane and the chlorine is dropped or displaced from the catalyst and enters into reaction with the pentane. The particles of catalyst, stripped of their chlorine, fall back to the bottom of the large tube, in the space between it and the percolator, and are again picked up by the chlorine jet and forced through the percolator, thus being used over and over.

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[92] U. S. Patent 1,308,760, July 8, 1919; assigned to Roessler and Hasslacher Chemical Co.; *J.S.C.I.*, 1919, 38, 676A.

[93] U. S. Patent 1,380,067, May 31, 1921; *Chem. Abs.*, 1921, 15, 3393; Koch, U. S. Patent 1,432,761, Oct. 24, 1922; *Chem. Abs.*, 1923, 17, 289; both patents assigned to Ohio Fuel Supply Co.

[94] *Ind. Eng. Chem.*, 1927, 19, 442.

Any vapors given off while the reaction is in progress pass into a refrigerated condenser and are refluxed back into the reaction tube. Some of the hydrogen chloride vapors pass through the condenser into a washer, where they are absorbed to form a dilute solution of hydrochloric acid.

Chlorination is stopped when the chlorinated derivatives are about 20 to 25 per cent of the total volume of hydrocarbons being treated. This is necessary in order to keep the formation of di- and trichloride derivatives at a minimum. Using the apparatus as described above, Koch and Burrell were able to carry the reaction to this point in about an hour to an hour and a quarter. In actual plant practice the recoveries of chloropentane were about 78 per cent, with an average conversion to amyl chloride of about 19 per cent.

The chlorinated hydrocarbons prepared in this manner contain a large proportion of hydrogen chloride and must be washed and neutralized before being fractionated to recover the amyl chloride. This is done by using a 10 to 20 per cent caustic solution followed by two or three washes with pure water. The washed hydrocarbon is then run into the fractionating still. The first fraction consists of untreated pentane and is retained for further chlorination. The amyl chloride cut is the fraction distilling between 90° and 110° C. This fraction amounts to approximately 25 per cent of the original charge, depending upon the degree of conversion during chlorination, and is about 80 per cent pure amyl chloride. The residue amounting to about 5 per cent consists principally of the di- and trichloro derivatives.

Several other processes of this same general type have been developed. For instance, Blanc[95] proposed the chlorination of liquid paraffin hydrocarbons with moist chlorine in the presence of actinic light and also a halogen carrier such as ferric chloride. Gasoline can be chlorinated in the presence of a solid catalyst such as aluminum or molybdenum chloride and ammonium carbonate;[96] or, after the removal of the heavy ends, it can be treated with chlorine in the presence of carbon tetrachloride, about 1 per cent aqueous ammonia and a metallic chloride such as aluminum or ferric chloride.[97] In the latter case the product is principally heptachlorohexane.

[95] U. S. Patent 1,248,065, Nov. 27, 1917; assigned to Goodyear Tire and Rubber Co.; *J.S.C.I.*, 1918, 37, 74A.

[96] Vivas, U. S. Patent 1,733,842, Oct. 29, 1929; assigned to International Fireproof Products Corp.; *Chem. Abs.*, 1930, 24, 512.

[97] Vivas, U. S. Patent 1,733,843, Oct. 29, 1929; *Chem. Abs.*, 1930, 24, 512; also British Patent 286,726, 1928; *Brit. Chem. Abs.* B, 1929, 349; both patents assigned to International Fireproof Products Corp.

In the process developed by Payne and Montgomery[98] the catalyst is first prepared by mixing a paraffin distillate (initial boiling point of about 450° F.) with powdered coal and completely chlorinating the mixture. Moist hydrocarbon gases, such as natural gas or pressure still gases, together with chlorine in the proportion of 3 volumes of gas to 1 volume of chlorine are passed over this catalyst at 300° F. The mixture is next passed through quartz tubes exposed to rays from a mercury vapor lamp in order to complete the chlorination. The liquid products are then condensed, and the remaining gases are cooled to obtain methyl chloride. Very little uncombined chlorine is found among the products.

The direct chlorination of hydrocarbons by passing vapors mixed with chlorine over a heated graphite catalyst has also been proposed.[99]

Thermal Chlorination. An interesting process for the thermal vapor phase chlorination of n- and iso-pentanes to amyl chlorides is the one described by Ayres.[100] The chemistry of this process has been previously discussed so that only the technical aspects of the operation need be considered here. The pentanes which were used were obtained as a narrow cut fraction (95 per cent boiling between 28° and 39° C.) of natural gasoline containing approximately equal proportions of normal and isopentanes. The scale of operations to which this process has been developed may be gaged by the following details which have been supplied by Ayres. Twenty-two tons of chlorine per day are fed into a flowing stream of hot pentane vapor. The daily throughput of pentane is of the order of 100,000 gallons though owing to the very short time of reaction (2.5 seconds) only about 3 gallons of pentane and 8 ounces of chlorine are present in the reaction zone at any given moment.

A general outline of plant operation has been supplied by Clark.[101] As indicated in the flow sheet in Figure 30, the pentane cut is pumped from storage to a mixing tank, where pentanes recovered from the system are added and the mixture is thoroughly dehydrated. From the mixing tank the pentanes are passed through a vaporizer. Chlorine is passed through another vaporizer and the two gas streams are combined in a mixing throat. From this they pass immediately into a gas-fired pipe still.

The exit gases from the pipe still pass through pipe banks cooled with a water spray and enter the first of four continuous fractionating columns. The first column is operated to take off an overhead product containing only pentanes and the hydrogen chloride produced in the chlorination. This product is returned to the mixing tank at the start of the system, while the bottom product, a mixture of amyl chlorides and unchlorinated pentanes, is pumped to the second continuous column. The pentane-rich overhead product from this column is returned to the feed of the first column, while the bottom product, low in pentanes and high in chlorides, passes to the third column. In the latter column the amyl dichlorides and more highly chlorinated substances are removed in the still liquor and sent to a separate discontinuous still, and the amyl chlorides are sent to the fourth column. Here a practically pure mixture of amyl chlorides is obtained as a bottom product, while the residual pentanes are taken off overhead together with some amyl chlorides and are returned to the feed of the first still.

The dichlorides and polychlorides in the still liquor from the third column are worked up in batches in a caustic still, only the dichlorides being recovered. The more highly chlorinated compounds are discarded.

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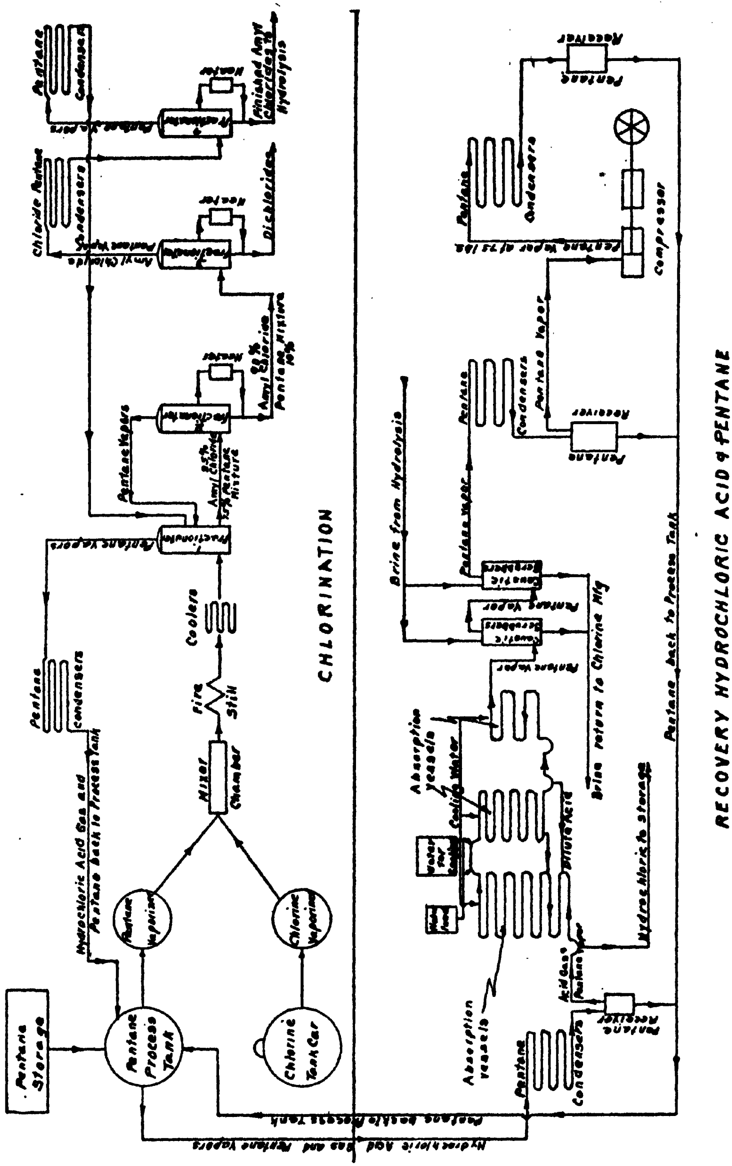
[98] U. S. Patent 1,453,766, May 1, 1923; assigned to Standard Oil Co. of Indiana; *J.S.C.I.*, 1923, 42, 800A.

[99] French Patent 605,950, 1925; *Brit. Chem. Abs.* B, 1928, 921.

[100] *Ind. Eng. Chem.*, 1929, 21, 899.

[101] *Ind. Eng. Chem.*, 1930, 22, 439.



CHLORINATION

RECOVERY HYDROCHLORIC ACID & PENTANE

Courtesy Industrial and Engineering Chemistry

FIG. 30.—Flowsheet for Industrial Chlorination of Pentane and Recovery of Hydrochloric Acid. (Clark.)

The recovery of the hydrogen chloride produced during the chlorination process is carried out as follows: This substance, together with unchlorinated pentanes, constitutes the overhead product from the first continuous still and is returned to the mixing tank at the start of the chlorination system, as shown in Figure 30. Here it is introduced at the bottom, and the dry hydrogen chloride, bubbling up through the liquid pentanes, combines with any water present to form hydrochloric acid, which settles out at the bottom of the tank and is drawn off from time to time. Only a fraction of the hydrogen chloride is removed in this way, the rest being recovered in a continuous system which withdraws gas from the top of the mixing tank, passes it through a condenser to remove most of the pentanes, and then through a double countercurrent absorption system of fused silica, where the hydrogen chloride is taken up in water. The exit gases from the absorption system are scrubbed with dilute caustic brine liquor from the subsequent hydrolysis operations and, after passing through a condenser, are compressed and condensed. The liquid pentanes are returned to the mixing tank.

An alternative procedure[102] for the recovery of hydrogen chloride is as follows: The gases leaving the reaction chamber, which are at a temperature of 275° C. or higher and under a pressure of 15 to 25 pounds, are led through a rectifier which is kept at a temperature just low enough to condense the chlorinated hydrocarbons and yet to allow the unreacted hydrocarbons and the hydrogen chloride to pass on. These latter gases are then passed through a condenser, which partially separates the hydrocarbons, and finally through an absorber. The temperature of the absorber is high enough, regulated by the rate at which water is fed to it, to prevent the condensation of the hydrocarbon gases and at the same time secure practically complete extraction of the hydrogen chloride.

Other processes for the thermal chlorination of hydrocarbons are those developed by Ayres[103] and by the Bataafsche Petroleum Maatschappij.[104] In the former process the hydrocarbon vapors together with small volumes of chlorine are heated to 315° to 370° C. for very short periods of time in the absence of any catalyst or illumination. In the latter process pentanes can be either brominated or chlorinated by heating the vapors mixed with bromine or chlorine in the dark to 250° to 330° C. To control chlorination of hydrocarbons such as pentane and avoid explosion, Lunt[104a] proposed to bring together chlorine under a pressure of 4 to 5 atmospheres and pentane vapor under about the same pressure in a mixing chamber at a lower pressure (about 2.6 atmospheres).

CHLORINATION OF HIGHER PARAFFIN HYDROCARBONS

The chlorination of paraffin hydrocarbons of six or more carbon atoms has been carried out either on mixtures of isomeric hydrocarbons or on petroleum fractions of narrow boiling range. Since usually very little information has been obtained regarding the constitution of even the monochlorinated products, on the whole our exact knowledge of the chlorination of the higher paraffins is extremely limited, and much work needs to be performed before any generalizations can be formulated. It appears, however, that the higher paraffins can be readily chlorinated either in the liquid or gaseous phases in the presence of diffused daylight or of catalysts, such as iodine. Chlorination in bright sunlight usually leads to intensive action resulting in carbon deposition. Most of the workers in this field have endeavored to restrict the chlorination process to the monochloro-derivatives, e.g., by carrying out the process in the absence of catalysts and stopping it as soon as somewhat less than the theoretical amount of chlorine required for monochlorination had been absorbed. As a rule catalysts tend to favor the production of polychlorinated products. Though the monochloro-compounds have been most generally produced, there is no difficulty in carrying the chlorination much further.

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[102] The hydrogen chloride can also be extracted from such a mixture by contacting the mixture in the vapor phase under pressure with water. The formation of a film of chlorinated hydrocarbons on the surface of the water is thus prevented, according to Ayres (U. S. Patent 1,831,474, Nov. 10, 1931; assigned to B. A. S. Co.), and the efficiency of the extraction is increased.

[103] U. S. Patent 1,717,136, June 11, 1929; *Chem. Abs.*, 1929, **23**, 3713; British Patent 320,406, 1928; *Chem. Abs.*, 1930, **24**, 2468; U. S. Patent 1,741,393, Dec. 31, 1929; *Chem. Abs.*, 1930, **24**, 1119; French Patent 657,518, June 16, 1928; *Chem. Abs.*, 1929, **23**, 4228; Canadian Patent 278,537, 1928; all patents assigned to B. A. S. Co. Ayres (U. S. Patent 1,835,202, Dec. 8, 1931; assigned to B. A. S. Co.; *Brit. Chem. Abs.* **B**, 1932, 878) suggests dehydrating the hydrocarbons before chlorination by treating them with dry hydrogen chloride. Amylene dichloride can be used in a paint-removing composition (Wilson, U. S. Patent 1,918,224, July 11, 1933; assigned to Sharples Solvents Corp.; *Chem. Abs.*, 1933, **27**, 4642) or for removing road tar from vehicles (Valee, U. S. Patent 1,913,647, June 13, 1933; assigned to Sharples Solvents Corp.; *Chem. Abs.*, 1933, **27**, 4364).

[104] British Patent 338,742, 1929; *Brit. Chem. Abs.* **B**, 1931, 237.

[104a] U. S. Patent 1,824,558, Sept. 22, 1931; assigned to E. B. Badger and Sons Co.; *Chem. Abs.*, 1932, **26**, 150.

The methods employed for chlorinating the higher paraffins are largely modifications of Schorlemmer's classical series of experiments on the chlorination of hexane. Schorlemmer[105] employed the following four methods of chlorination: (1) chlorination of the cooled liquid hydrocarbon in diffused daylight; (2) chlorination in the liquid phase in the presence of iodine; (3) chlorine alone passed into the vapors of the boiling hydrocarbon; and (4) chlorination in the vapor phase in the presence of iodine vapor. In all four cases the bulk of the products consisted of a mixture of primary and secondary monochlorohexanes but it was noted that liquid phase chlorination tended to result in the production of large quantities of polychloro-derivatives. Thus Schorlemmer obtained a hexachlorohexane by passing chlorine into hexane from petroleum as long as any action could be observed, first in diffused daylight and afterwards in direct sunlight.

Morgan[106] reported that on the vapor phase chlorination of hexane, obtained from petroleum naphtha, about nine-tenths was converted into a mixture of monochlorides boiling from 124° to 130° C., the remainder consisting of more highly chlorinated products. Passage of chlorine into boiling hexane, according to Michael and Turner,[107] yielded a mixture of chlorohexanes, of which about 10 per cent was 1-chlorohexane. A small amount of 2-chlorohexane, and less of 3-chlorohexane, was formed at the same time.

The vapor phase chlorination of both n-hexane and isohexane (obtained from Pennsylvania straight run gasoline) in the presence of diffused light was investigated by Faragher and Garner.[108] In both instances the products consisted principally of a mixture of monochlorinated hydrocarbons, together with small quantities of dichloro and higher chlorinated compounds. From the chlorinated n-hexane a fraction (boiling point 120° to 124° C.) was obtained which corresponded in properties to 2-chlorohexane.

On subjecting boiling diisopropyl to chlorination the chief product formed, according to Schorlemmer,[109] was a monochloride boiling at 127° C. In the presence of iodine a dichloride melting at 160° C. was the main product. Silva[110] observed, however, that when diisopropyl was chlorinated in the presence of sunlight two monochlorides were formed; one boiling at 122° C. and the other at 118° C. Aschan[111] obtained two monochlorides from the diisopropyl fraction of

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[105] *Ber.*, 1870, 3, 615; *Phil. Trans.*, 1872, 162, 112; *Proc. Roy. Soc. (London)*, 1871, 19, 20; *Phil. Trans.*, 1872, 162, 116, 118; *Ann.*, 1872, 161, 265, 272, 275.

[106] *Chem. News*, 1874, 30, 292; *Chem. Soc. Abs.*, 1875, 28, 301; *Ann.*, 1875, 177, 304.

[107] *Ber.*, 1906, 39, 2153.

[108] *J.A.C.S.*, 1921, 43, 1717.

[109] *Proc. Roy. Soc. (London)*, 1867, 16, 35; *Ann.*, 1867, 144, 186; *Z. für Chemie*, 1867, 10, 1, 75.

[110] *Ber.*, 1872, 5, 984; *ibid.*, 1873, 6, 36; *ibid.*, 1874, 7, 953.

[111] *Ber.*, 1898, 31, 1802; *Översikt. Finska Vetenskaps-Soc. Förh.*, 1915, 58, 122; *Chem. Abs.*, 1920, 14, 3654.

Baku petroleum (boiling range 57° to 59° C.), one boiling at 117° to 119° C. and considered to be a tertiary chloride, and the other boiling at 123° to 125° C. was unidentified.

Heptanes. Chlorination of heptane[112] in the liquid phase and in the presence of diffused daylight yielded a monochloro-product boiling at 150° C., and a dichloro-product boiling at 190° C. The vapor phase chlorination of heptane from *Pinus sabiniana,* however, resulted in the formation of 1-chloro- and 2-chloropentane. Principally mixtures of monochloro-derivatives of heptane have been obtained on the chlorination of the appropriate petroleum fraction by Pelouze and Cahours,[113] Morgan,[114] and Faragher and Garner.[115] The last-named investigators were also able to isolate a dichloroheptane fraction boiling at 90° to 100° C. at 15 mm. pressure from their products.

Isoheptane, prepared from ethyl and isoamyl bromides, was chlorinated by Grimshaw.[116] This was done in the vapor phase and in diffused illumination. The latter condition was necessary in order to control the reaction. The products consisted of monochlorides, together with small quantities of higher chlorinated products.

Octanes. Very little work has been done with pure octane, the initial material in most instances being a petroleum fraction with a very narrow boiling range. Only in rare instances have the structures of the chlorinated products been determined.

From a petroleum fraction boiling at 122° to 125° C. Schorlemmer[117] prepared an octyl chloride boiling at 173° to 176° C. By conversion to the corresponding alcohol it was shown to be principally 2-chlorooctane. Previously he had noted the formation of monochlorooctane, boiling point 170° to 172° C., by the action of chlorine on octane. Monochlorooctanes of about this same boiling range, 172° to 176° C., have been made from petroleum fractions by Pelouze and Cahours[118] and by Mabery and Hudson.[119] n-Octyl chloride, boiling at 182° C., was obtained by Cahours and Demarcay[120] by the chlorination of an octane formed during the distillation of crude fatty acids with superheated steam.

Schorlemmer[121] observed the formation of a monochloro-compound boiling at 165° C. on the chlorination of diisobutyl. Carleton-Williams[122] noted the formation of a mixture of primary and secondary chlorides when diisobutyl was chlorinated in the vapor phase in the presence of sunlight, but was unable to effect separation of the products by fractional distillation.

Rather energetic chlorination of diisoamyl has been reported by Hartmann.[123] The treatment consists first in chlorinating in the cold with chlorine, then with antimony pentachloride in sealed tubes at 190° to 200° C., and finally a second treatment with antimony pentachloride at 450° C. Under such conditions the products were tetrachloromethane and hexachlorobenzene, together with a small quantity of hexachlorobutadiene.

[112] Schorlemmer, *Proc. Roy. Soc. (London)*, 1865, **14**, 169, 466, 468; *Ann.*, 1865, **136**, 259, 266.

[113] *Compt. rend.*, 1862, **54**, 1241; *ibid.*, 1863, **56**, 505; *ibid.*, 1863, **57**, 62; *Ann. chim. phys.*, 1864, (4) 1, 1; *J. prakt. Chem.*, 1863, **88**, 314; *ibid.*, 1863, **89**, 359; *ibid.*, 1864, **91**, 98.

[114] *Loc. cit.*

[115] *Loc. cit.*

[116] *Ber.*, 1877, **10**, 1602; *J.C.S.*, 1877, **32**, 260.

[117] *Proc. Roy. Soc. (London)*, 1869, **18**, 25; *Ann.*, 1869, **152**, 153.

[118] *Loc. cit.*

[119] *Amer. Chem. J.*, 1897, **19**, 243.

[120] *Compt. rend.*, 1875, **80**, 1568.

[121] *Proc. Roy. Soc. (London)*, 1867, **16**, 35; *Ann.*, 1867, **144**, 186.

[122] *J.C.S.*, 1877, **31**, 542; *ibid.*, 1879, **35**, 126.

[123] *Ber.*, 1891, **24**, 1011.

Nonanes. Monochloro-derivatives of this hydrocarbon were prepared by Pelouze and Cahours[124] and by Lemoine[125] from nonane isolated from petroleum fractions. Chlorination was effected by passing chlorine into the gently heated hydrocarbon.

Thorpe and Young[126] passed chlorine into purified nonane in the presence of direct sunlight. Vigorous reaction took place, and occasionally the passage of chlorine was stopped and the mixture distilled. The portion distilling below 200° C.

TABLE 121.—*Products of Chlorination of the Higher Paraffins.*

Hydrocarbon	Source of Hydrocarbon	Conditions of Chlorination	Products
n-Hexane	Synthetic petroleum	Vapor phase	Primary and secondary monochlorides, b.p. 125°-130° C.[a]
	Petroleum	Chlorination in diffused daylight	Monochlorohexanes, b.p. 125°-128° C.[b]
	Petroleum	Vapor phase	90% of monochloro-compounds, b.p. 120°-134° C.[c]
	——	Liquid phase at b.p. in diffused daylight	1-,2-, and 3-chlorohexanes.[d]
	Petroleum	Vapor phase	Monochloride, b.p. 120°-124° C. (2-chloro-compound?)[e]
	——	Further chlorination of monochlorides in diffused daylight	Dichlorohexane, b.p. 180°-184° C. Trichlorohexane, b.p. 215°-218° C. Tetra- and hexachlorohexanes.[b]
Isohexane	Petroleum (b.p. 61°-64° C.)	Vapor phase	Mixture of monochlorides, b.p. 119°-123° C.[e]
Diisopropyl (2,3-Dimethylbutane)	Synthetic	Liquid phase in cold	Two monochlorides, b.p. 122° and 118° C., also a dichloride of b.p. 160° C.[e, f]
	From Baku petroleum (b.p. 57°-59° C.)	Liquid phase at 0° C.	Three monochlorides, the one of b.p. 117°-119° C. being the tertiary compound.[g]
n-Heptane	Synthetic	Liquid phase in diffused daylight	A monochloride, b.p. 150° C. and a dichloride, b.p. 190° C.[h]
	From *Pinus sabiniana*	Vapor phase	Mixture of 1-chloro- and 2-chloro-heptanes, boiling at 143°-157° C.[i]
	Petroleum (b.p. 92°-94° C.)	Chlorine passed into warm liquid hydrocarbon	Monochlorides, b.p. 148°-152° C.[j]
	Petroleum (b.p. 96°-99° C.)		Monochlorides, b.p. 144°-156° C.[k]
	Petroleum (b.p. 97°-100° C.)	Liquid phase at 20°-25° C.	Monochloride, b.p. 150°-160° C., and a dichloride, b.p. 90°-100° at 15 mm.[l]
Isoheptane (2-methylhexane)	Synthetic	Vapor phase in weak illumination	Almost entirely monochlorides, b.p. 140°-150° C., with small amounts of higher chlorinated products.[m]

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[124] *Loc. cit.*

[125] *Bull. soc. chim.*, 1884, (1) 41, 163.

[126] *Proc. Roy. Soc. (London)*, 1873, 21, 196; *Ann.*, 1873, 165, 20; *Chem. Soc. Abs.*, 1873, 26, 260.

TABLE 121.—*Products of Chlorination of the Higher Paraffins (continued).*

Hydrocarbon	Source of Hydrocarbon	Conditions of Chlorination	Products
n-Octane	Petroleum (b.p. 122°–125° C.)		Monochloride, b.p. 173°–176° (2-chloro-?).[n]
	Synthetic		Monochlorides, b.p. 174°–176° C., consisting of primary with small amount of secondary.[n]
	Synthetic		1-chloro-octane, b.p. 182° C.[o]
	Petroleum (b.p. 119.5°–120° C.)	Vapor phase	Monochlorides, b.p. 164°–166° C.[p]
	Petroleum (b.p. 124°–125° C.)	Vapor phase	Monochlorides, b.p. 173°–176° C.[p]
Diisobutyl (2,5-Dimethylhexane)	Synthetic	Vapor phase in diffused sunlight	Chloro-octane, b.p. 165° C. $d^{10.5}$ 0.8834[q]
	Synthetic	Vapor phase in diffused sunlight	Mixture of primary and secondary monochlorides.[r]
Nonanes	Synthetic	Liquid phase in sunlight	A mixture of primary and secondary monochlorides, b.p. 190°–198° C., together with higher chlorinated products.[s]
	Petroleum (b.p. 136°–138° C.)	Liquid phase, warm	Monochloride, b.p. 196° C.[t]
	Synthetic (b.p. 132° C. at 759 mm).	Liquid phase, below 65° C.	Monochloride, b.p. 180°–184° C.[u]
Decanes	Both synthetic and decanes from petroleum fractions	Liquid and gaseous phases in diffused sunlight, etc.	Monochlorodecanes and dichlorodecane of unknown structure; chlorination vigorous even in diffused light.[v]
Undecanes	Petroleum	Liquid phase in diffused sunlight	Monochlorundecane, b.p. 225°–230° C. at 747 m., and (possibly) dichlorundecane.[w]
Dodecane	Petroleum	Liquid phase	Monochlorododecanes and dichlorododecanes.[w]

[a] Schorlemmer, previous citations.
[b] Pelouze and Cahours, *loc. cit.*
[c] Morgan, *J.C.S.*, 1875, **28**, 302; *Ann.*, 1875, **177**, 304.
[d] Michael and Turner, *Ber.*, 1906, **39**, 2153.
[e] Faragher and Garner, *J.A.C.S.*, 1921, **43**, 1717.
[f] Silva, *loc. cit.*
[g] Aschan, *Ber.*, 1898, **31**, 1802; *Chem. Abs.*, 1920, **14**, 3654.
[h] Schorlemmer, *Proc. Roy. Soc. (London)*, 1865, **14**, 169, 466, 468; *Ann.*, 1865, **136**, 259, 266.
[i] Schorlemmer and Thorpe, *Phil. Trans.*, 1884, **174**, 269; *Ann.*, 1883, **217**, 149; *Amer. Chem. J.*, 1884, **6**, 28.
[j] Pelouze and Cahours, *loc. cit.*
[k] Morgan, *J.C.S.*, 1875, **28**, 301; *Ann.*, 1875, **177**, 304.
[l] Faragher and Garner, *J.A.C.S.*, 1921, **43**, 1717.
[m] Grimshaw, *J.C.S.*, 1873, **26**, 312, 318; *Ann.*, 1873, **166**, 163.
[n] Schorlemmer, *Proc. Roy. Soc. (London)*, 1869-70, **18**, 25; *Ann.*, 1869, **152**, 153.
[o] Cahours and Demarcay, *Compt. rend.*, 1875, **80**, 1568.
[p] Mabery, *Amer. Chem. J.*, 1897, **19**, 419; *Chem. Soc. Abs.*, 1897, **72** (1), 449.
[q] Schorlemmer, *Proc. Roy. Soc. (London)*, 1867, **16**, 35; *Ann.*, 1867, **144**, 186.
[r] Carleton-Williams, *J.C.S.*, 1877, **31**, 542; *ibid.*, 1879, **35**, 126.
[s] Thorpe and Young, *Proc. Roy. Soc. (London)*, 1873, **21**, 196; *Ann.*, 1873, **165**, 20.
[t] Pelouze and Cahours, *loc. cit.*
[u] Lemoine, *loc. cit.*
[v] Mabery, *loc. cit.*; Pelouze and Cahours, *loc. cit.*; Lemoine, *loc. cit.*; Grimshaw, *loc. cit.*; Schorlemmer, *loc. cit.*; Schütz and Hartogh, *Ber.*, 1909, **42**, 3611; Cloez, *Compt. rend.*, 1877, **85**, 1004; Wurtz, *Compt. rend.*, 1863, **56**, 1167, 1246; *Ann.*, 1863, **128**, 231.
[w] Mabery, *loc. cit.*; Pelouze and Cahours, *loc. cit.*

was again subjected to chlorination. This procedure was adopted to avoid as far as possible the formation of higher chlorinated products. Upon completion of chlorination the product was distilled and a nonyl chloride fraction boiling at 190° to 198° C. obtained. This fraction, however, was thought to be a mixture of primary and secondary monochlorononanes.

Decanes, Undecanes and Dodecanes. Decyl chlorides have been prepared by Mabery[127] from petroleum fractions boiling at 173° to 174° C. and from different crude petroleums. Chlorination was effected in diffused light, and the products were separated by fractionation. The monochloro-derivatives generally boiled around 130° to 140° C. at 80 mm., and the dichloro-derivatives at 160° to 170° C. at 80 mm. The monochloro-derivatives of undecane, boiling at 225° to 230° C. in 747 mm., were obtained in a similar manner. Indications were also obtained that some dichloro-derivatives were formed at the same time. Monochlorododecane boiled at 142° to 153° C. at 80 mm., while a possible dichloro-derivative boiled at 150° to 160° C. at 80 mm.

A résumé of the most important contributions on the chlorination of paraffin hydrocarbons from hexane to dodecane, as compiled by Egloff, Schaad and Lowry,[128] is given in Table 121.

The chlorination of kerosene, from Pennsylvania petroleum, by means of antimony pentachloride in the presence of iodine and at 350° to 360° C. has been reported by Hartmann.[129] The products of such chlorination were stated to be principally hexachloroethane and hexachlorobenzene, together with small quantities of tetrachloromethane and perchloromesole (hexachlorobutadiene, C_4Cl_6). Using another fraction (boiling at 300° to 350° C.) of this same petroleum and chlorinating at 450° C. with antimony pentachloride the products were almost entirely tetrachloromethane and hexachlorobenzene.

The chlorination of various petroleum fractions corresponding with tridecane, tetradecane, pentadecane, hexadecane, heptadecane and octadecane has been described by Mabery and also by Pelouze and Cahours but the data available are fragmentary. These higher paraffins appear to chlorinate very readily in diffused daylight at room temperatures and monochloro-derivatives (which are probably mixtures of isomers) have been obtained. In the case of paraffins with more than 17 carbon atoms, it is stated that chlorination proceeds readily without catalysts.[129a] The chlorination of the higher paraffins has been mainly investigated from the viewpoint of the subsequent dechlorination of the monochlorides so obtained, to yield drying oils of unsaturated character. The olefins produced by the removal of hydrogen chloride from monochlorinated products of paraffin wax may be oxidized to fatty acids which are of value in the manufacture of soaps. The chlorination of paraffin wax for the ultimate production of fatty acids by the latter series of processes has been described by Schaarschmidt and Thiele.[130] These workers found that when chlorine is passed into liquid paraffin at 160° C. the gas is completely utilized and the operation proceeds without external heating. The process is interrupted when the requisite gain in weight has been attained. Chlorination does not occur quite uniformly and, in addition to isomeric monochloro-derivatives, dichloro-products are also formed before all the paraffin is attacked.

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[127] *Amer. Chem. J.*, 1897, 19, 419; Mabery and Hudson, *Amer. Chem. J.*, 1897, 19, 482.

[128] *Chem. Reviews*, 1931, 8, 1.

[129] *Ber.*, 1891, 24, 1019.

[129a] Gardner and Bielouss, *Ind. Eng. Chem.*, 1922, 14, 619.

[130] *Ber.*, 1920, 53B, 2128.

A series of chlorinated paraffins varying in chlorine content from 20 to 48.5 per cent was prepared by Gardner[130a] by bubbling dry chlorine through paraffin wax at a temperature of about 70° C. Introduction of more than 40 per cent of chlorine is accomplished with difficulty. The relationship between chlorine content and density, congealing point, viscosity, and surface tension was examined. Viscosity increases sharply after more than 40 per cent chlorine has combined. As the chlorine content increases the congealing point drops to a minimum (at about 37 per cent chlorine in these experiments) and then increases sharply.

UTILIZATION OF CHLORO-DERIVATIVES OF HIGHER PARAFFINS

A number of industrial methods dealing with the chlorination of the immediate homologues of the pentanes have been dealt with previously. Most of the methods for the chlorination of higher paraffins have for their object the utilization of the monochlorinated products as raw materials in the manufacture of fatty acids, drying oils, and similar materials.

According to Perkin, Weizmann and Davies,[131] n-heptane may be chlorinated in the liquid phase at 90° C. under the influence of ultraviolet radiations. The chlorination process may also be accelerated by catalysts such as phosphorus compounds or iodine. Thus, when chlorine was passed into 300 grams of heptane until the increase in weight was 50 grams the products consisted of 225 grams of monochloroheptanes and 10 grams of dichloroheptanes.

Strauss[132] stated that the higher paraffin hydrocarbons, such as undecane and dodecane, or petroleum fractions corresponding with these hydrocarbons or their mixtures, could be converted mainly into monochloro-derivatives by vapor phase chlorination under diminished pressure at a temperature approximately double that of the boiling point of the hydrocarbon. A controlled quantity of chlorine was employed and the reaction was catalyzed by the addition of a small amount of iodine vapor.

The chlorination of the higher paraffins to yield highly chlorinated substances (useful as coating or impregnating materials or for varnishing) is described by Buchner,[133] who proposed to pass chlorine into a solution of the hydrocarbon in carbon tetrachloride at ordinary or elevated temperatures and under the influence of chemically active radiation. The carbon tetrachloride is said to exert a definite accelerating action. Many of the products are solid non-plastic substances melting at 100° to 115° C. Introduction of chlorine into a solution of paraffin in carbon tetrachloride at 70° to 75° C. yielded a material containing 77 per cent of chlorine.

The use of chlorinated hydrocarbons in the preparation of flame-proof insulation has been described by Ellis. One method[134] consists in chlorinating solvent naphtha until about 40 to 50 per cent of chlorine by weight has been absorbed, and a crystalline product separates from the mother-liquor. This crystalline chlorinated product is then incorporated with wax, asphalt or similar combustible organic insulating material and imparts to the latter flame-proof qualities. Such a composition is suitable, for example, for use on copper wire. Another method[135] of preparing such compositions is by chlorination of heavy petroleum, for example an "asphaltic oil" such as Mexican petroleum, and incorporating a sufficient quantity of the chlorinated product with a plastic insulating material so as to render the composition flame-proof. Waxes, such as paraffin wax, ceresin wax or Japan wax, can be chlorinated until the quantity of chlorine absorbed is 10 per cent or more. Such chlorinated substances, either alone, admixed with the chlorinated compounds described in the two previous examples, or incorporated with asphalts, pitches, malthas or similar substances, furnish flame-proof insulating materials.[136]

[130a] *Ind. Eng. Chem.*, 1933, **25**, 1211.

[131] British Patent 22,653, 1912; *J.S.C.I.*, 1913, **32**, 1029.

[132] German Patent 267,204, 1912; *Chem. Zentr.*, 1913, **2**, 2013.

[133] U. S. Patent 1,129,165, Feb. 23, 1916; *Chem. Abs.*, 1915, **9**, 1128.

[134] Ellis, U. S. Patent 1,248,638, Dec. 4, 1917; *Chem. Abs.*, 1918, **12**, 412.

Thiele[137] described a method of making drying oils, to be used as linseed oil substitutes, from kerosenes containing large proportions of cyclic hydrocarbons. The first stage in the process is chlorination with moist chlorine.

Deschauer[138] has reported the chlorination of montan wax to yield highly chlorinated products, which may resemble fossil resins, such as copals, when their chlorine content is sufficiently high. He introduced chlorine into a warm mixture of the liquid wax and dilute alkali (10 per cent caustic soda). Chlorinated products of montan wax are claimed to be excellent substitutes for beeswax, i.e., for insulation purposes or floor polish. By changing the chlorine content of the products, their properties may be varied.

In the preservation of fruit while in transit, to the market the fruit is first treated with a mold-inhibiting agent, such as a solution of sodium hypochlorite containing sodium bicarbonate, and then, while still wet, with a shrinkage-retarding film of a coating material which includes "chlorocosane." Chlorocosane, which is made by completely chlorinating paraffin wax, melting point 145° F., contains about 40 to 50 per cent chlorine, and has the consistency of a heavy oil.[139]

The use of chloroparaffin resin as a chewing-gum base has been described by Geller.[140] Examples are: (1) a mixture of soft chloroparaffin resin, hard chloroparaffin resin, and a small proportion of depolymerized rubber; (2) a mixture of fat, fatty acids, chloroparaffin resin and rubber.

Schrauth[141] described the preparation of dry, odorless soaps, soluble in hot water and forming an abundant lather, by alkali fusion of the chlorination products of petroleum fractions. The chlorination is carried only to the monochloro-stage and the monochloro-derivatives are then subjected to alkali fusion at 200° to 300° C. for 6 to 8 hours. Hydrogen is evolved during the process. Under these conditions cetyl chloride yields palmitic acid.

Bosshard and Strauss[142] described the production of certain derivatives (e.g., arylalkyl ethers) from the halogenated aliphatic saturated hydrocarbons containing at least 16 carbon atoms. Thus a *monochloroparaffin* of melting point 35° to 40° C., produced by chlorination of paraffin wax, may readily be condensed with phenol and alkali carbonate to yield *phenoxyparaffin,* a soap-like mass of melting point 60° C., the sulphonic acid of which may be used in tanning. Similarly a dichloroparaffin (melting point 40° to 60° C.) may be condensed with phenol to furnish a *phenoxychloroparaffin.*

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[135] Ellis, U. S. Patent 1,246,809, Nov. 13, 1917; assigned to New Jersey Testing Laboratories; *Chem. Abs.,* 1918, 12, 298.

[136] Ellis, U. S. Patent 1,246,810, Nov. 13, 1917; assigned to New Jersey Testing Laboratories; *Chem. Abs.,* 1918, 12, 298.

[137] U. S. Patent 1,254,866, Jan. 29, 1918; *Chem. Abs.,* 1918, 12, 769.

[138] U. S. Patent 1,429,932, Sept. 26, 1922; *Chem. Abs.,* 1922, 16, 4084.

[139] McDill, U. S. Patent 1,836,267, Dec. 15, 1931; assigned to Food Machinery Corp.; *Brit. Chem. Abs.* **B**, 1932, 912. Carbon tetrachloride mixed with paraffin has been suggested for this same purpose (McDill, U. S. Patent 1,900,295, Mar. 7, 1932; assigned to Food Machinery Corp.; *Chem. Abs.,* 1933, 27, 3015).

[140] U. S. Patents 1,855,016 and 1,855,017, Apr. 19, 1932; both patents assigned to American Chicle Co.; *Chem. Abs.,* 1932, 26, 3346.

[141] German Patent 327,048, 1914; *J.S.C.I.,* 1921, 40, 227A.

[142] German Patent 344,878, 1918; assigned to Elektrochem. Werke G.m.b.H.; *Chem. Abs.,* 1923, 17, 1243.

The preparation and properties of a synthetic hydrocarbon oil formed by the condensation of a monochlorinated wax and an aromatic hydrocarbon has been described by Davis.[143] The paraffin wax is chlorinated by passing chlorine through it until the chlorine content of the wax is about 10 to 12 per cent. During chlorination the temperature should be above 140° F., but should not exceed 300° F. The chlorinated product is then slowly added to a mixture of equal weights of an aromatic hydrocarbon (e.g., benzene, naphthalene or anthracene) and aluminum chloride. To keep the mixture well stirred during the addition of the chlorinated wax it is necessary that some inert solvent, such as kerosene, should be present and during this operation the temperature is maintained at 140° to 160° F. After the reaction is completed the aluminum chloride sludge is withdrawn and the kerosene and unreacted wax are removed by distillation, using reduced pressures for the latter. The addition of small proportions of the hydrocarbon oil so prepared to wax-bearing lubricating oils greatly reduces the pour point of the latter, thereby eliminating the necessity for severe dewaxing operations. As an example, the addition of 1 per cent of the synthetic hydrocarbon oil to a lubricating oil (from a Pennsylvania crude petroleum) lowered its pour point from 30° F. to below —5° F.

The work of Gardner and Bielouss[144] on the production of drying oils from chlorinated products of higher petroleum fractions is of interest. The chlorination of the high boiling liquid paraffin hydrocarbons was found to proceed smoothly in the absence of catalysts. The chlorinated products may then be dechlorinated by heating to 250° C. without the addition of any catalysts, under which conditions complete removal of chlorine, as hydrogen chloride, can be effected. The products consist of olefins mixed with cyclic hydrocarbons produced by ring closure during the dechlorination. According to Gardner,[145] excellent drying oils are produced by heating chlorinated hydrocarbons, containing 30 to 54 per cent of chlorine, to 240° to 320° C. for periods of 0.5 to 8 hours with small amounts of rosin and fatty acids from linseed oil. During the heating, the chlorine is removed as hydrogen chloride, some water passes off, and the acid number of the reaction mixture decreases continuously. Bielouss[146] stated that a satisfactory drying oil can be made by dechlorinating at 240° C. or lower without a catalyst. Also by successive chlorination and nitration of a mineral oil distillate, of specific gravity not less than 0.882, products are obtained of use in varnishes or pyroxylin compositions.[147]

The chlorination of higher petroleum fractions immediately after these hydrocarbons have been subjected to thermal decomposition has been reported by Messenger[148] to yield chlorohydrocarbons suitable as solvents and raw materials for synthesis. This process, however, is not strictly a substitutive chlorination of saturated hydrocarbons but rather an addition of chlorine to unsaturated hydrocarbons produced by the preliminary pyrolytic treatment.

Lilienfeld[148a] treated cellulose xanthate with di- or poly-halogenated paraffins in which at least 2 halogens are attached to a carbon atom (for example, 1,1-dichloroethane, 1,1-dichlorodimethylmethane) to produce artificial threads. The cellulose xanthate is prepared by xanthating alkali-cellulose which has been treated with a hydroxyalkylating agent such as ethylene chlorohydrin.[148b]

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[143] U. S. Patent 1,815,022, July 14, 1931; assigned to Standard Oil Development Co. For a discussion of effects of this synthetic hydrocarbon oil, or "Paraflow," on lubricating oils, see Davis and Blackwood, *Ind. Eng. Chem.*, 1931, **23**, 1452; Davis, *National Petroleum News*, 1932, **24** (52), 32, 34; *Chem. Abs.*, 1933, **27**, 1494; *cf.* Suida and Pöll, *Petroleum Z.*, 1933, **29** (23), 23; *Motorenbetr.*, 1933, **6**, 2; *Brit. Chem. Abs.* **B**, 1933, 691.

[144] *Ind. Eng. Chem.*, 1922, **14**, 619; U. S. Patent 1,384,447, July 12, 1921; *J.S.C.I.*, 1921, **40**, 667A.

[145] U. S. Patent 1,412,399, Apr. 11, 1922; *Chem. Abs.*, 1922, **16**, 2233.

[146] U. S. Patent 1,384,423, June 12, 1921; *J.S.C.I.*, 1921, **40**, 66A.

[147] Bielouss, U. S. Patent 1,519,017, Dec. 9, 1924; *Chem. Abs.*, 1925, **19**, 575.

[148] U. S. Patent 1,623,061, Apr. 5, 1927; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1927, **21**, 1660.

[148a] British Patent 357,121, 1930; *Brit. Chem. Abs.* **B**, 1932, 141.

Cone, Davidson and Laucks[149] suggested a mixture of a halogenated paraffin hydrocarbon and a dispersed vegetable protein, such as soya-bean protein, as a suitable water-resistant adhesive, while the I. G. Farbenindustrie A.-G.[150] proposed the manufacture of materials capable of being used as lubricant and greasing agents in the textile and leather industries, by treating halogenated mixtures of paraffin hydrocarbons, containing more than 8 carbon atoms and at least 2 halogen atoms, with caustic alkalies, alkali carbonates or alkaline earths.

Insecticides have been prepared by Goulenko[150a] by mixing chlorinated petroleum compounds with terpenes. Pirard[150b] used a stain-removing composition prepared from crude chlorinated petroleum hydrocarbons, aromatic hydrocarbons, and ether.

BROMINATION OF HIGHER PARAFFINS

From an industrial standpoint, the bromination of paraffin hydrocarbons of 6 or more carbon atoms is of little interest. The available data on this subject are very incomplete and only in a few cases have definite chemical individuals been isolated among the products. Bromine reacts with these hydrocarbons either very slowly or not at all in the cold, but in sunlight, at higher temperatures, and in the presence of catalysts, reaction is more rapid. In all cases bromination is much slower than chlorination.

Hexanes. Monobromides, and dibromo-compounds as well, have been produced from n-hexane. Michael and Garner,[151] using Schorlemmer's method, dropped bromine slowly into the upper part of a reflux condenser while hexane was kept boiling in an attached flask. Reaction took place immediately in sunlight and the main product, boiling at 143° to 146° C., consisted of 2-bromohexane and 3-bromohexane together with some higher boiling products. Herzfelder[152] obtained hexabromohexane by bromination of n-hexane at its boiling point in the presence of iron wire, while Pelouze and Cahours[153] prepared a dibromohexane, boiling point 210° to 212° C., by bromination of liquid n-hexane.

By the bromination of 2,3-dimethylbutane (diisopropyl) at a mild temperature and in sunlight, Silva[154] obtained a crystalline dibromo-compound but no monobromide was isolated.

Heptanes. The bromination of heptane appears to proceed more readily than in the case of the lower paraffins, and the main initial product appears to be a 2-bromoheptane, though more highly brominated products are also obtained. Bromination does not occur in the dark even in the presence of catalysts but the process is rapid at 100° C. or in sunlight. The most complete investigation of this reaction is due to Venable,[155] who used n-heptane from *Pinus sabiniana.* For the production of optimum yields of monobromo-compounds, less than the theoretical amount of bromine was added, as rapidly as it was absorbed, to the gently boiling hydrocarbon. Distillation of the products yielded unchanged heptane, a main fraction of heptyl bromide (25 to 30 per cent of the theoretical), and higher boiling products of polybromo-compounds and their decomposition products. This fraction was difficult to examine on account of its instability. The monobromo-compound fraction, boiling at 165° to 167° C., appeared to be identical with the 2-bromoheptane previously isolated by Schorlemmer. Later attempts to increase the yield of secondary monobromide were unsuccessful.[156]

[148b] Lilienfeld, British Patent 335,906, 1929; *Brit. Chem. Abs.* **B**, 1931, 153.

[149] U. S. Patent 1,726,510, Aug. 27, 1929; assigned to Laucks, Inc.; *Chem. Abs.*, 1929, **23**, 5018.

[150] British Patent 343,948, 1929; *Brit. Chem. Abs.* **B**, 1931, 578.

[150a] French Patent 662,256, 1928; *Chem. Abs.*, 1930, **24**, 458.

[150b] Belgian Patent 377,278, 1931; *Chem. Abs.*, 1932, **26**, 1406.

[151] *Ber.*, 1901, **34**, 4036.

[152] *Ber.*, 1893, **26**, 2432.

[153] *J. pr. Chem.*, 1863, **88**, 314; **89**, 359.

[154] *Ber.*, 1872, **5**, 984; 1873, **6**, 36.

[155] *Ber.*, 1880, **13**, 1650; *Amer. Chem. J.*, 1888, **10**, 237.

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[156] Wheeler, *J.A.C.S.*, 1903, **25**, 532.

Chapter 31

Halogenation of Cycloparaffins

The reactions of the cycloparaffin hydrocarbons, containing five- and six-membered carbon rings, with halogens are markedly similar to those of the straight chain paraffins and lead to the production of substitution products containing one or more halogen atoms. Not only are these reactions of the cycloparaffins and paraffins similar in kind but they are also often strikingly alike in degree. Thus, for example, cyclohexane exhibits a degree of reactivity to chlorine and bromine similar to that of n-hexane. In the case of cyclopropane and cyclobutane and their homologues, the substitutive halogenation reaction has also been observed but it is frequently associated with an *addition reaction* leading to the formation of halogenated derivatives of straight chain hydrocarbons and thus involving the rupture of the somewhat unstable three- and four-membered carbon rings. Since however the predominating cycloparaffinic hydrocarbons occurring in crude petroleum, at least in so far as their chemical constitution has been determined, appear to be those possessing cyclopentane or cyclohexane rings, attention is specially directed to the halogenation reactions of these types in the following account.

Perhaps the most striking aspect of the subject of halogenation of these hydrocarbons is the extremely limited character of the information available. Much work on the halogenation of five- and six-membered cycloparaffin hydrocarbons has been carried out with petroleum fractions of doubtful homogeneity while the conditions of halogenation are often incompletely specified. Moreover in relatively few instances have even the primary products of halogenation been definitely identified. Though more work has been carried out on cyclohexane and its immediate homologues, the halogenation reactions of the cyclopentane hydrocarbons, and even of cyclopentane itself, have never been subjected to more than a superficial examination. Under such circumstances, therefore, any account of the halogenation reactions of these hydrocarbons must, of necessity, be quite inadequate. Nevertheless, it has been deemed advisable to collect the available information on this subject in the hope that this long-neglected field of research will be subjected to further investigation. Not only would a more complete investigation of the halogenation reactions of the simple cyclopentane and cyclohexane hydrocarbons be of considerable scientific interest, but it might also open up avenues of technical exploitation of such hydrocarbons, for example, in the production of cyclic secondary alcohols and their derivatives.

Despite the extreme meagerness and oftentimes lack of specificity of much of the work on the halogenation of the cyclopentane and cyclohexane hydrocarbons, the available information permits of a few generalizations. Chlorination appears to take place much more readily than bromination especially in the presence of sunlight or other actinic light. As in the case of the paraffin hydrocarbons, the reaction appears to be of a cumulative nature, prolonged treatment favoring the formation of polychlorinated products. The presence of catalysts also favors multiple substitution. By operating in the presence of actinic light either in the liquid or gaseous phases it appears possible to obtain considerable proportions of monochlorinated products. Mixtures of monochlorinated products of the homologues of cyclohexane have been obtained but the composition of such mixtures has been investigated only in the case of methylcyclohexane. According to the work of Sabatier and Mailhe on the chlorination of this hydrocarbon, monochlorination results in the introduction of chlorine atoms into the ring with the production of both 3- and 2-chloro compounds as well as a trace of the 4-chloro compound. Dichloro and higher chlorinated compounds have also been produced by the direct chlorination of cyclohexane and a number of its homologues but the constitutions of these products have not been determined.

The cyclopentane and cyclohexane hydrocarbons appear to be relatively resistant to the action of bromine. At temperatures above 100° C., however, bromine attacks many of these hydrocarbons with the formation of bromo-derivatives but no monobromides have been definitely obtained. In the presence of catalysts, such as aluminum bromide or iron wire, bromination takes place more readily and, in the presence of excess of bromine, frequently converts cyclohexane hydrocarbons into polybrominated derivatives of the corresponding benzenoid hydrocarbon.

CYCLOPROPANE AND ITS HOMOLOGUES

The photochemical chlorination of cyclopropane has been studied by Gustavson,[1] who found that, though no chlorination occurred in the dark, in direct sunlight the reaction is explosive. Accordingly Gustavson effected the chlorination of cyclopropane in diffused daylight over water in a cooled container. The compounds produced under these conditions included not only mono- and di-chlorinated cyclopropane derivatives but also chlorinated derivatives of propane, showing that there is a tendency for the cyclopropane ring to be ruptured. The straight chain chlorinated products actually found were 1,3-dichloropropane, 1,1,3-trichloropropane, and a relatively small amount of 1,2,3-trichloropropane.[2] *Monochlorocyclopropane* produced by the photochemical chlorination process, was obtained as a liquid of pleasant odor, boiling point 43° C. at 744 mm.[3] On heating the compound with potassium acetate and glacial acetic acid, quantities of allyl acetate were obtained,[4] while it was more readily brominated by bromine in a sealed tube at 16° to 18° C. than dichlorocyclopropane. The *dichlorocyclopropane* obtained in the photochemical chlorination of cyclopropane[5] was considered by Gustavson to be 1,1-dichlorocyclopropane since it could be brominated in sunlight to furnish 2,2-dichloro-1,3-dibromopropane. This bromination reaction is another example of the relative ease with which the cyclopropane ring is ruptured under the influence of chemical reagents. 1,1-Dichlorocyclopropane is a colorless liquid of boiling point 75° C. at 746 mm. and d^{15}_{4} 1.206. It exhibits a much greater stability than monochlorocyclopropane and is not decomposed by metallic sodium at 140° C.

The halogenation of cyclopropane in diffused daylight may be summarized in the following scheme:

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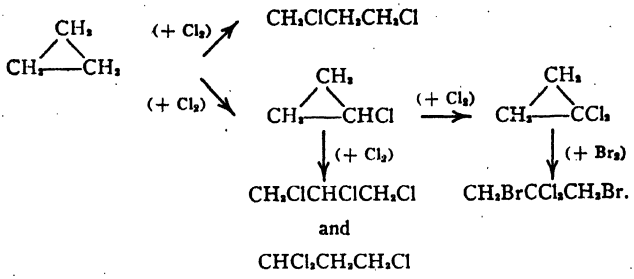
[1] *J. pr. Chem.*, 1890, (2) **42**, 495; *Chem. Soc. Abs.*, 1891, **60**, 159.
[2] Gustavson, *J. pr. Chem.*, 1894, (2) **50**, 380.
[3] Gustavson, *J. pr. Chem.*, 1891, (2) **43**, 396.
[4] Gustavson, *J. pr. Chem.*, 1892, (2) **46**, 159.
[5] Gustavson, *J. pr. Chem.*, 1890, (2) **42**, 495.



The bromination of cyclopropane has been the object of much study, particularly by Gustavson. In the presence of sunlight, combination of bromine with cyclopropane, either in the dry or moist condition, takes place very rapidly with the production of 1,3-dibromopropane as the sole product.[6] In the dark the bromination of perfectly dry cyclopropane at room temperature proceeds very slowly but the reaction is markedly accelerated by the presence of moisture[7] or of certain bromine carriers, including aluminum halides, ferric chloride, zinc chloride, and elemental iodine. In the presence of hydrogen bromide, which may also act as a catalyst for bromination, the reaction products consist of 1,3- and 1,2-dibromopropanes and their bromination products, as well as some propyl bromide;[8] but when aluminum bromide or ferric chloride is used as catalyst, 1,2-dibromopropane is the predominating material.[9] It is evident, therefore, that the main reaction involved in the action of bromine on cyclopropane is the rupture of the three-carbon ring system with subsequent bromination of the unsaturated system momentarily formed.

Under the influence of halogens, and particularly of bromine, a number of the homologues of cyclopropane undergo simultaneous ring rupture and halogenation with the formation of straight chain derivatives. Thus, bromination of *methylcyclopropane* in the absence of light leads mainly to 1,3-dibromobutane besides, possibly, 1-bromo-1-methylcyclopropane and 1,3,3-tribromobutane.[10] Similarly, the action of bromine on *1,1-dimethylcyclopropane* yields trimethylethylene dibromide.[11]

Cyclobutane. Apparently very little is known about the halogenation of the cyclobutane series of hydrocarbons, though cyclobutane is stated to be stable to bromine in chloroform in the cold.[12] In the bromination of the dihalogen derivatives of cyclobutane, the marked tendency for the occurrence of rupture of the carbon ring system, previously noticed in the case of cyclopropane derivatives, is also observable. Thus, 1,2-dichloro-cyclobutane is converted by heating with bromine at 60° C., and later at 100° to 110° C. in the presence of iron powder, into a mixture of dichlorodibromo-butane, dichlorotribromo-butane, and dichlorotetrabromo-butane. Similarly, 1,2-dibromo-cyclobutane may be brominated by heating with bromine in the presence of iron powder, or of iodine, to furnish a mixture of polybrominated butanes.

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[6] Gustavson, *J. pr. Chem.*, 1900, (2) **62**, 294.
[7] Gustavson, *J. pr. Chem.*, 1900, (2) **62**, 273, 287.
[8] Gustavson, *J. pr. Chem.*, 1900, (2) **62**, 273. Freund, *Monatsh.*, 1882, **3**, 628; *J. pr. Chem.*, 1882, (2) **26**, 370.
[9] Gustavson, *J. pr. Chem.*, 1900, (2) **62**, 290.
[10] Demjanow, *J. Russ. Phys.-Chem. Soc.*, 1902, **34**, 217; *Chem. Zentr.*, 1902, **1**, 1277.
[11] Gustavson and Popper, *J. pr. Chem.*, 1898, (2) **58**, 458; *Chem. Soc. Abs.*, 1899, **76** (1), 263; Gustavson, *J. pr. Chem.*, 1900, (2) **62**, 270; *Chem. Soc. Abs.*, 1901, **80** (1), 61.
[12] Willstätter and Bruce, *Ber.*, 1907, **40**, 3989.

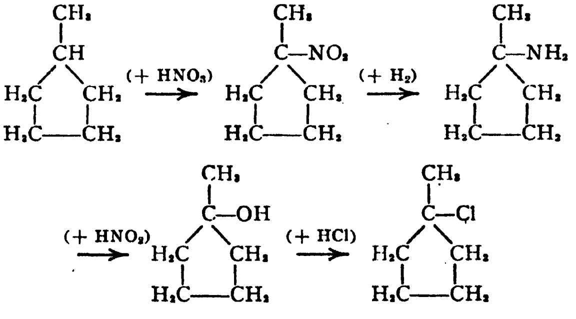
CYCLOPENTANE

There is apparently no published record of an experimental investigation of the chlorination of cyclopentane. In view of the undoubted presence of this hydrocarbon in many crude petroleums, a careful study of its halogenation reactions may prove of interest. A number of chlorinated cyclopentanes have been obtained indirectly, e.g., monochlorocyclopentane from cyclopentanol and hydrogen chloride;[13] a trichloro-compound from chlorocyclopentene; and a tetrachloride by chlorination of cyclopentadiene in chloroform solution at —15° C.[14]

Although cyclopentane is inert to bromine in the dark, exposure of a mixture of bromine and this hydrocarbon to sunlight results in substitution, with evolution of hydrogen bromide, at about the same rate as in the case of n-pentane. Even at 100° C. the dark reaction with bromine in a sealed tube is very slow but at 128° to 130° C. the reaction is more rapid and leads to the production of bromination products together with some carbon deposition.[15]

METHYLCYCLOPENTANE

Very little is known of the halogenation reaction of the homologues of cyclopentane. Markownikow[16] observed that methylcyclopentane was energetically chlorinated on introducing chlorine into the hydrocarbon at ordinary temperature and in diffused daylight. A mixture of chlorides was obtained but no definite individual compound could be isolated. Markownikow synthesized the tertiary monochloride, i.e., 1-chloro-1-methylcyclopentane, by means of the following series of reactions, starting with the tertiary nitro-compound.



The tertiary monochloride was obtained as a liquid (boiling point 97° C. at 349 mm., or 122° to 123° C. at 757 mm.) which was partly decomposed at higher temperatures with the evolution of hydrogen chloride and the production of an unsaturated hydrocarbon of the formula C_6H_{10}.

Another monochloride was also synthesized by Markownikow by the following series of steps, starting with the tertiary alcohol:

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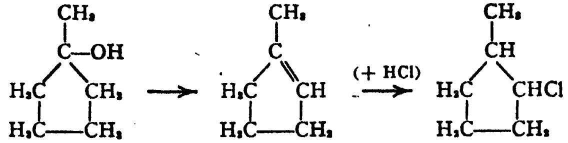
[13] Zelinsky, *Ber.*, 1908, 41, 2627.
[14] Kraemer and Spilker, *Ber.*, 1896, 29, 555.
[15] Wislicenus and Hentzschel, *Ann.*, 1893, 275, 322.
[16] *Ann.*, 1899, 307, 335.



The resulting monochloride, namely 2-chloro-1-methylcyclopentane, boiled at 126° S. and had d_0^0 0.9281.

CYCLOHEXANE

Chlorination. The chlorination of cyclohexane has been the subject of a number of important researches. Markownikow [17] obtained *monochlorocyclohexane*, a liquid boiling at 142° C. at 750 mm., by the action of moist chlorine on the cold hydrocarbon in diffused sunlight. When dry chlorine gas was employed it became necessary to heat the hydrocarbon to near its boiling point in order to obtain a reaction but this procedure also resulted in the formation of polychloroderivatives. On fractionating the less volatile products from the chlorination of cyclohexane Markownikow was able to isolate what he considered to be two isomeric *dichlorocyclohexanes*, one boiling at 192° to 194° C. and having d_{15}^{15} 1.167, and the other of boiling point 196° to 198° C. and d_{15}^{15} 1.172.

A careful examination of the chlorination of cyclohexane has been recorded by Fortey.[18] The hydrocarbon was placed in a reflux apparatus together with a small quantity of iron filings and exposed to direct sunlight while a current of dry chlorine was passed through the liquid at room temperature. The reaction commenced in about one-quarter hour, the liquid became warm, and hydrogen chloride was evolved. After several hours the product was washed and yielded on distillation under reduced pressure a mixture of dichloro-derivatives, boiling point 110° to 115° C.; trichloro-compounds, boiling point 135° to 140° C.; and tetrachloro-derivatives, boiling point 160° to 165° C.; all under 30 mm. pressure. No monochlorinated cyclohexane was produced by Fortey on chlorination in the presence of the iron catalyst. The monochloride, however, was prepared, together with dichloro-cyclohexanes, by passing dry chlorine into cyclohexane in the cold in diffused daylight. Chlorination in the dark could not be effected while the application of heat or the employment of chlorine carriers (catalysts) gave rise to the formation of higher substitution products such as di-, tri-, and tetra-chlorocyclohexanes. Fortey observed that when chlorine was passed into cyclohexane in diffused daylight in the cold, it dissolved, forming initially a yellow solution; at a certain stage, combination began, heat was developed, and hydrogen chloride evolved. If from this point, chlorine was passed slowly for about 3 hours, a good yield of the monochloride was obtained.[19] The product was washed with sodium carbonate solution, then with water, and dried over calcium chloride and finally distilled. Monochlorocyclohexane was the fraction boiling at 141.3° to 141.6° C. at 768 mm., and having d_0^0 0.991. A purified dichlorocyclohexane fraction boiled at 193° to 194° C. while a third fraction boiling very constantly at 201° to 202° C. also gave analytical figures in agreement with those required by a dichloride. It appears very probable that the direct chlorination of cyclohexane furnishes more than one dichlorocyclohexane.

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[17] *Ann.*, 1898, 302, 1.

[18] *J.C.S.*, 1898, 73, 932.

[19] Similar observations were made by Schorlemmer (*Ann.*, 1877, 188, 250) in the case of the chlorination of isoheptane. The results obtained by Fortey may be explained on the basis of the chain mechanism theory of the chlorination of saturated hydrocarbons and the known inhibiting effects of traces of oxygen. After the oxygen has been used up in breaking reaction chains the inhibitory effect disappears. (Hass, private communication.)

Sabatier and Mailhe[20] carried out the chlorination of cyclohexane (prepared by the catalytic hydrogenation of benzene) by the passage of chlorine into the hydrocarbon cooled to 0° C. in diffused sunlight. Energetic substitution was found to take place under these conditions with the production of mono-, di-, tri-, and tetrachlorinated products. The presence of iodine monochloride or antimony chloride exerted no influence on the reaction but aluminum chloride caused the formation of condensed products. Fractionation of the products of the chlorination of cyclohexane in diffused light at 0° C. yielded the following: (a) A monochlorocyclohexane, boiling point 141.6° to 142.6° C. at 749 mm. and having d_0^0 1.0161. (b) Two isomeric dichlorocyclohexanes; one boiling in two equal fractions at 105.4° to 106.4° C. (d_0^0 1.2056) and 106.4° to 107.4° C. at 50 mm. (d_0^0 1.2060), and the other boiling at 112.4° to 113.4° C. at 50 mm. (d_0^0 1.2222). The latter is probably a 1,2-dichloride. (c) Two *liquid* trichlorocyclohexanes, boiling at 139.5° to 141.5° C. at 50 mm. (d_0^0 1.3535) and 143.5° to 145.5° C. at 50 mm. (d_0^0 1.3611), as well as a *solid* trichlorocyclohexane of melting point 66° C., boiling point 150.4° to 151.4° C. at 50 mm., and d_0^0 1.5103. The latter compound is probably a symmetrical, or 1,3,5-trichloro-derivative, since it yielded benzene on heating with alcoholic potash at 100° C.

The continued action of chlorine on cyclohexane in sunlight led to the formation of a liquid and a solid tetrachloro-compound. The solid tetrachloride was crystalline and melted at 173° C.

Using Sabatier and Mailhe's method of chlorination, Faragher and Garner[21] converted cyclohexane into a mixture of the mono- (boiling point 139° to 144° C. and d_0^{20} 1.002), di- (boiling point 75° to 85° C. at 15 mm., and d_0^{20} 1.179), and tri-chlorides (boiling point 96° to 105° C. at 15 mm. and d_0^{20} 1.266).

The properties of the mono- and di-chlorides are of considerable interest. Monochlorocyclohexane may be readily converted into cyclohexene, with elimination of hydrogen chloride, by heating that chlorohydrocarbon with quinoline or alcoholic potash, and, to lesser extent, with silver oxide or silver acetate. The best yield of cyclohexene was obtained by Fortey by refluxing it with quinoline for 7 to 8 hours. The elimination of hydrogen chloride can also be accomplished by vapor phase decomposition with or without catalysts. With metallic magnesium in dry ethereal solution monochlorocyclohexane yields, besides dicyclohexyl, a Grignard compound which can be converted into a carboxylic acid[22] or a sulphonic acid[23] by decomposition with carbon dioxide or sulphur dioxide, respectively.

The higher chlorinated cyclohexanes are also decomposed by hot alkalies with the production of unsaturated or benzenoid substances. Cyclohexadiene was obtained by Fortey by distilling dichlorocyclohexane with quinoline. The solid trichlorocyclohexane yielded benzene on being heated with alcoholic potash under pressure at 100° C. while under similar conditions solid tetrachlorocyclohexane was converted into chlorobenzene.

Bromination of Cyclohexane. According to Markownikow,[24] bromine reacts with cyclohexane in sealed tubes at 110° C., but the monobromo-compound is not produced. When the halogen and hydrocarbon are employed in molecular proportions about 50 per cent of the hydrocarbon remains unchanged, the remainder being converted into polybrominated products. In the presence of aluminum bromide a product is formed which melts at 120° to 121° C. and is apparently a mixture of the compounds $C_6H_2Br_8$ and $C_6H_3Br_7$. This product was identical with that previously obtained by Kistner from methylpentamethylene, bromine and aluminum bromide, and probably represents a conversion of the hexamethylene into the pentamethylene ring. Fortey was unable to isolate any definite bromination products from the action of bromine on cyclohexane but produced pure monobromocyclohexane by the combination of cyclohexane and hydrogen bromide.

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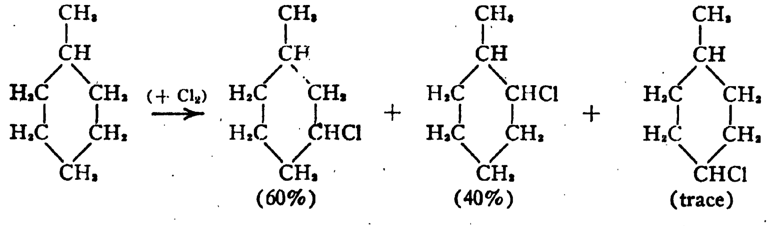
[20] *Compt. rend.*, 1903, **137**, 240; *Bull. soc. chim.*, 1903, (3) **29**, 976; *Ann. chim.*, 1907, (8) **10**, 531.
[21] *J.A.C.S.*, 1921, **43**, 1715.
[22] Sabatier and Mailhe, *Ann. chim.*, 1907, (8) **10**, 535; *Chem. Abs.*, 1908, **2**, 793.
[23] Borsche and Lange, *Ber.*, 1905, **38**, 2766.
[24] *Ann.*, 1898, **302**, 1; *Chem. Soc. Abs.*, 1899, **76** (1), 22.

At higher temperatures and on prolonged treatment, cyclohexane is converted by bromine into brominated derivatives of benzene. Zelinsky[25] obtained symmetrical 1,2,4,5-tetrabromobenzene by heating 2 grams of cyclohexane and 36 grams of dry bromine in a sealed tube at 150° C. and finally at 200° C. for several days.

METHYLCYCLOHEXANE

Chlorination. The chlorination of methylcyclohexane was examined by Markownikow[26] and was considered by him to give rise to a mixture of the tertiary monochloride, 1-chloro-1-methylcyclohexane, boiling point 148° to 151° at 752 mm. (with decomposition), together with another chloride boiling at 155.5° to 157.7° C. under 740 mm. pressure. Almost simultaneously, Sabatier and Mailhe[27] made a careful examination of the mixed monochlorides, boiling point 157° to 159° C., produced by the chlorination of methylcyclohexane at ordinary temperatures. To ascertain the nature of the products formed in this chlorination, Sabatier and Mailhe prepared all of the five possible monochloro-derivatives and, from the data obtained, concluded that neither 1-chloro-1-methylcyclohexane nor hexahydrobenzyl chloride was present in the chlorinated product. The mixture of monochlorides prepared by the direct chlorination of methylcyclohexane was converted by Grignard's method into the magnesium methylcyclohexyl chlorides, which, on prolonged oxidation in a current of pure dry oxygen followed by treatment with cold water, gave the alcohols corresponding with the chloro-derivatives. From the results of the examination of these alcohols, it was concluded that the monochlorides formed in the direct chlorination of methylcyclohexane consist of about 40 per cent 2-chloro-1-methylcyclohexane, and about 60 per cent 3-chloro-1-methylcyclohexane, together with a small proportion of 4-chloro-1-methylcyclohexane.



Like other monohalides of the cycloparaffins, the monochloro methylcyclohexanes may be readily decomposed to yield hydrogen chloride and the corresponding methylcyclohexene. The tertiary chloride is particularly readily decomposable and cannot be distilled at ordinary pressure without profound decomposition into an olefin and hydrogen chloride. These monochlorides readily yield Grignard compounds which on treatment with carbon dioxide are converted into carboxylic acids.[28]

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[25] *Ber.*, 1901, 34, 2799.
[26] *Ann.*, 1905, 341, 118; *J. Russ. Phys.-Chem. Soc.*, 1903, 35, 1042. See also Spindler, *J. Russ. Phys.-Chem. Soc.*, 1891, 23, 41; *Ber.*, 1891, 24, Ref. 561.
[27] *Compt. rend.*, 1905, 140, 840; *Chem. Soc. Abs.*, 1905, 88 (1), 334.

Bromination. According to Markownikow,[29] methylcyclohexane is resistant to the action of bromine in diffused light. Even in direct sunlight at temperatures of about 100° C., bromine exerts only a slow reaction on the hydrocarbon but bromination occurs readily at 115° C. In the presence of aluminum bromide, dry bromine reacts readily with methylcyclohexane forming pentabromotoluene.[29, 30]

CHLORINATION OF THE HIGHER HOMOLOGUES OF CYCLOHEXANE

From a fraction of Balachany (Caucasian) gasoline with a boiling range from 116° to 120° C., Markownikow and Oglobin[30a] isolated *1,3-dimethylcyclohexane,* the constitution of which was proved by its nitration to trinitro-m-xylene and by its conversion to m-xylene on heating with sulphur at 220° C. The chlorination of this hydrocarbon was studied by employing Schorlemmer's method.[31] Besides a dichloride fraction boiling at 225° to 235° C. a mixture of monochlorides of the formula $C_8H_{15}Cl$ was also produced. Fractionation of the monochloride mixture resulted in the separation of the following fractions, which were thought to be isomeric substances but were of doubtful homogeneity:[32]

Monochloride, boiling point 174° to 176° C., d_{20}^{20} 0.9374.

Monochloride, boiling point 169° to 171° C., d_{20}^{20} 0.9247.

None of the other isomeric dimethylcyclohexanes seems to have been chlorinated but an *isooctanaphthene,* C_8H_{16}, of unknown structure was isolated by Putochin[33] from Caucasian light petroleum. Chlorination of this hydrocarbon was found by Pautinsky[34] to result in the production of a mixture of monochlorides, which was fractionated to give two fractions, one of boiling point 176° to 179° C. and d_0^0 0.9680, and the other of boiling point 179° to 182° C. and d_0^0 0.9734. Here again the chemical homogeneity of these preparations is very doubtful.

Of the cyclohexane homologues with nine carbon atoms (nonanaphthenes), *1,2,4-trimethyl-cyclohexane* was isolated by Markownikow and Oglobin and also by Konowalow[35] from Caucasian petroleum. The same hydrocarbon was also found by Ahrens and von Mozdzenski[36] in the xylene fraction of high temperature coal tar. Konowalow chlorinated his specimen of this hydrocarbon (boiling point 135° to 137° C.) in the vapor phase, employing dry reagents and obtained a mixture of *monochlorides* which was resolved into two fractions by distillation, together with a dichloride fraction, boiling at 230° to 235° C. One fraction of the monochloride boiled at 185° to 187° C. and the other at 182° to 184° C. The dichloride, d_0^0 1.1035, on heating with sodium acetate and acetic acid for five hours at 200° C. yielded considerable amounts of an unsaturated hydrocarbon[37] of the formula C_9H_{14}.

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[28] Gutt, *Ber.*, 1907, **40**, 2065.
[29] Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1903, **35**, 1033; *Ann.*, 1905, **341**, 130.
[30] Kursanow, *Ber.*, 1899, **32**, 2972.
[30a] *J. Russ. Phys.-Chem. Soc.*, 1883, **15**, 332; *Ber.*, 1883, **16**, 1877; see Chapter 1.
[31] Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1884, **16**, 294; *Ber.*, 1885, **18**. Ref. 186.
[32] Shukowski, *J. Russ. Phys.-Chem. Soc.*, 1897, **27**, 303.
[33] See Markownikow, *Ber.*, 1884, **18**, Ref. 186.
[34] Dissertation Moscow, 1886, mentioned by Aschan, "Chemie der alicyclischen Verbindungen," 1905, p. 606.
[35] *J. Russ. Phys.-Chem. Soc.*, 1890, **22**, 118.
[36] *Z. angew. Chem.*, 1908, **21**, 1411.

Ahrens and von Mozdzenski[38] also submitted a specimen of *1,2,4-trimethylcyclohexane* (isolated from the xylene fraction of coal tar) to chlorination in diffused daylight at 30° C. and obtained a mixture of monochlorides of the formula $C_9H_{17}Cl$, as a liquid of pungent odor boiling at 103° to 104° C. under 40 mm. and having d^{20}_4 0.9229. The constitution of these chlorinated products is quite unknown.

The chlorination of *decanaphthenes* ($C_{10}H_{20}$) of established constitution has been studied in one case, namely in that of p-menthane, or *1-methyl-4-isopropylcyclohexane*. Berkenheim[39] chlorinated this hydrocarbon in the vapor phase and obtained a liquid monochloride boiling at 208° to 210° C. and of d^0_0 0.9553. The constitution of this monochloride is unknown, and its homogeneity doubtful. A decanaphthene fraction of Caucasian petroleum boiling at 160° to 162° C. and designated *α-decanaphthene* by Zubkoff[40] was chlorinated in the presence of water. The products consisted of monochlorides (boiling point 206° to 209° C.), dichlorides (boiling point 160° to 165° C. at 60 mm.), as well as trichlorinated and higher chlorinated products. When heated with sodium acetate and acetic acid at 200° C. the monochloride fraction yielded an unsaturated hydrocarbon, $C_{10}H_8$, and also the acetate of a decanaphthenol, which could be hydrolyzed to the alcohol. The *dichloride* fraction was decomposed by heating with quinoline to furnish an unsaturated hydrocarbon of the formula $C_{20}H_{16}$, boiling at 162° to 170° C.

Another decanaphthene, called *β-decanaphthene*, boiling at 168.5° to 170° C. at 752 mm., has been isolated from Baku petroleum.[41] This hydrocarbon, which is probably identical with *1,3-dimethyl-5-ethylcyclohexane*, was converted by the action of moist chlorine into a mixture of (at least) two monochlorides as well as a dichloride.[42] The monochlorides, one of which boiled at 213° to 216° C. at 760 mm. and the other at 216° to 219° C. at the same pressure, were converted into the unsaturated decanaphthylene, $C_{10}H_{18}$, to the extent of 44 per cent and 76 per cent by heating with sodium acetate at 250° C. and with quinoline, respectively. The dichloride fraction boiled at 164° to 167° C. under 60 mm. pressure.

A few higher boiling petroleum fractions, corresponding in composition to some of the higher cycloparaffins but of unknown structure, have been subjected to chlorination. A fraction of Baku petroleum boiling at 179° to 181° C. and possessing the formula $C_{11}H_{22}$ (*undecanaphthene*) was chlorinated with dry chlorine, in the vapor phase at the temperature of its boiling point, and in the presence of sunlight; the resulting product was a mixture of isomeric *monochlorides* boiling at 210° to 225° C. This monochloride mixture could be converted mainly into an unsaturated hydrocarbon $C_{11}H_{20}$ (boiling point 166° to 180° C.) by heating with alcoholic potash and was decomposed by heating with water in a sealed tube.

Mabery and his collaborators[43] have chlorinated a number of high boiling fractions of Californian and Canadian petroleums having compositions agreeing with the formula C_nH_{2n}. Since these hydrocarbons were fully saturated, it must be concluded that they belong to the cycloparaffin series though their constitutions were not determined. Chlorination was effected in most cases by passing chlorine into the hydrocarbon material floating on water. Table 122 shows the results of Mabery and Sieplein[44] on the chlorination of various naphthenic constituents of Californian petroleum:

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[37] Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1891, **23**, 446.

[38] *Z. angew. Chem.*, 1908, **21**, 1411.

[39] *Ber.*, 1892, **25**, 686.

[40] *J. Russ. Phys.-Chem. Soc.*, 1893, **25**, 382.

[41] Zubkoff, *J. Russ. Phys.-Chem. Soc.*, 1893, **25**, 383.

[42] Rudewitsch, *J. pr. Chem.*, 1893, (2) **48**, 188; Markownikow and Rudewitsch, *J. Russ. Phys.-Chem. Soc.*, 1898, **30**, 586.

[43] Mabery, *Am. Chem. J.*, 1897, **19**, 419; *Chem. Soc. Abs.*, 1897, **72** (1), 449; Mabery and Sieplein, *Am. Chem. J.*, 1901, **25**, 284; *Chem. Soc. Abs.*, 1901, **80** (1), 306; *Am. Chem. J.*, 1905, **33**, 264; *Chem. Soc. Abs.*, 1905, **88** (1), 313.

TABLE 122.—*Chlorination of California Petroleum.*

		Chlorinated Product	
Hydrocarbon Fraction	Formula	B.P. ° C.	d^{20}_{4}
Dimethylcyclopentane(?)	$C_7H_{13}Cl$	147	0.9316
Methylcyclohexane	$C_7H_{13}Cl$	141–142	0.9310
Dimethylcyclohexane	$C_8H_{15}Cl$	168–170	0.9358
Trimethylcyclohexane	$C_9H_{17}Cl$	186–188	0.938
Decanaphthene	$C_{10}H_{19}Cl$	105–110 at 50 mm.	0.947
Undecanaphthene	$C_{11}H_{21}Cl$	125–130 at 50 mm.	0.9583
Dodecanaphthene	$C_{12}H_{23}Cl$	130–135 at 17 mm.	0.9616
Tridecanaphthene	$C_{13}H_{25}Cl$	140–145 at 17 mm.	0.9747
Tetradecanaphthene	$C_{14}H_{27}Cl$	150–155 at 13 mm.	0.9748 $\left\{d^{20}_{20}\right\}$
Pentadecanaphthene	$C_{15}H_{29}Cl$	170–175 at 14 mm.	0.9771 $\left\{d^{20}_{20}\right\}$

In a similar manner Mabery chlorinated a number of higher boiling fractions of Canadian petroleum, containing constituents of the formula C_nH_{2n} and presumably cycloparaffinic in nature. Table 123 shows the properties of the chlorides produced from various fractions corresponding to the formulas $C_{12}H_{24}$ to $C_{15}H_{30}$.

TABLE 123.—*Chlorination of Canadian Petroleum.*

Hydrocarbon Fraction		Chlorinated Product		
Formula	B.P. ° C.	Formula	B.P. ° C. at 15 mm.	d^{20}_{0}
$C_{12}H_{24}$	216	$C_{12}H_{23}Cl$	160	0.9145
$C_{13}H_{26}$	228–230	$C_{13}H_{25}Cl$	165	0.9221
$C_{14}H_{28}$	141–143 at 50 mm.	$C_{14}H_{27}Cl$ $C_{14}H_{26}Cl_2$	180 197–200	0.9288 1.0066
$C_{15}H_{30}$	159–160 at 50 mm.	$C_{15}H_{29}Cl$	190	0.9358

BROMINATION OF THE HIGHER HOMOLOGUES OF CYCLOHEXANE

Little is known regarding the bromination of the higher cyclohexane hydrocarbons in the absence of aluminum bromide or similar catalysts. At low temperatures bromine does not appear to react with these hydrocarbons while at higher temperatures polybrominated products and brominated derivatives of benzenoid hydrocarbons are produced. *1,3-Dimethylcyclohexane* does not react with bromine at room temperature[45] but, according to Knoevenagel and MacGarvey,[46] combination takes place with evolution of hydrogen bromide on warming. No monobrominated products of the cyclohexane hydrocarbons have been prepared by direct bromination.

In the presence of aluminum bromide as a catalyst, bromine reacts vigorously with the higher cyclohexane hydrocarbons to furnish good yields of polybrominated compounds corresponding to the analogous benzene hydrocarbon. Since these latter compounds are usually well-defined crystalline solids, this reaction affords a valuable general method of identifying cyclohexane hydrocarbons of unknown structure, and has been used extensively for this purpose.[47] Instead of aluminum bromide, iron powder is said to be quite satisfactory in the bromination of 1,2,4-trimethylcyclohexane to tribromopseudocumene.

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[44] Mabery and Sieplein, *Amer. Chem. J.*, 1901, **25**, 284.
[45] Aschan, *Ber.*, 1892, **24**, 2718.
[46] *Ann.*, 1897, **297**, 167.

The products of the bromination of various homologous cyclohexanes in the presence of aluminum bromide are given in Table 124.

TABLE 124.—*Bromination of Homologues of Cyclohexanes in the Presence of Aluminum Bromide.*

Cyclohexane Hydrocarbon	Brominated Product	
	Name	M.P. °C.
1,3-Dimethylcyclohexane	Tetrabromo-m-xylene	246
1,4-Dimethylcyclohexane	Tetrabromo-p-xylene	253
1,2,4-Trimethylcyclohexane	Tribromopseudocumene	234
1-Methyl-4-isopropylcyclohexane[a]	—	—
1,3-Dimethyl-5-ethylcyclohexane β-Decanaphthene	2,4,6-Tribromo-1,3-dimethyl-5-ethylbenzene[b]	218–220

[a] Berkenheim, *Ber.*, 1892, **25**, 686. The brominated product in this case was a viscous liquid which could not be crystallized.

[b] Markownikow and Rudewitsch, *J. Russ. Phys.-Chem. Soc.*, 1898, **30**, 588, 590; *Chem. Soc. Abs.*, 1899, **76** (1), 581.

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[47] For example, Morgan (*J.S.C.I.*, 1932, **51**, 67T) has employed this method in the identification of the cyclohexane derivatives in low temperature tars.

Chapter 32

Halogenation of Benzene and Its Immediate Homologues

The following account of the halogenation reactions of benzene and its homologues is necessarily a very brief résumé of a vast field which has received attention from a large number of investigators from the early days of organic chemistry until the present time. The chlorination reactions of these hydrocarbons are discussed more fully than those of bromination since the latter are at present of little significance from an industrial standpoint.

The technical applications of the chlorination reactions of aromatic monocyclic hydrocarbons are almost entirely centered around the production of monochlorobenzene from benzene and of benzyl and benzal chlorides from toluene. The pyrolysis of petroleum has also yielded aromatic hydrocarbons (Chapter 5). Hitherto, the only commercial source of aromatic hydrocarbons has been coal tar obtained by the high temperature carbonization of bituminous coal. The possibilities of utilizing certain petroleum fractions as sources of toluene were fully explored during the World War when large quantities of that hydrocarbon were extracted from certain petroleums for conversion into TNT. The extraction of individual aromatic hydrocarbons in a pure state from petroleum presents difficulties even when petroleum fractions very rich in aromatic constituents are available. Most of the work on the chlorination of aromatic hydrocarbons has been carried out on fairly pure materials and little is known as to the possibilities of using fractions of petroleum rich in aromatics as sources of chlorinated aromatic substances. In view of the greater reactivity of the aromatic hydrocarbons in the absence of light and in the presence of certain halogen carriers, the selective chlorination of the aromatic constituents of a mixture of such hydrocarbons and saturated hydrocarbons of the paraffin type appears to be a possibility. It would be of interest to determine to what extent it is possible to chlorinate benzene or toluene mixed with paraffinic hydrocarbons without the latter suffering chlorination.

Benzene reacts with halogens (bromine and chlorine) both by addition and by substitution, but toluene and the higher homologous alkylbenzenes undergo substitution almost exclusively. In the latter case, however, the substitution reaction can take place either in the aromatic nucleus or in the paraffinic side chain. The most remarkable feature of this field of halogenation is the extraordinary influence exerted by the conditions of reaction on the relative distribution of substitution between nucleus and side chains. The important factors operating in this way are temperature, illumination, catalysts, and also to a lesser degree the concentration of the reactants and the nature of the diluting medium, if any. Exposure to illumination and high temperatures favor substitution in the side chain, and low temperatures, absence of light, and, above all, the presence of the usual halogen carriers, promote nuclear substitution. Many halogen carriers, such as iodine, iron, or aluminum halides, exert such a powerful influence not only on the rate of nuclear substitution but also on the type of substitution that all other factors are completely nullified; no substitution whatever occurs in the side chain and the products are exclusively nuclear substituted derivatives.[1]

The mechanism of the action of halogen carriers seems to depend upon the formation of an addition compound with the halogen, which is then liberated under the conditions of halogenation in a more active state than before. This view is supported by the fact that aromatic hydrocarbons may be chlorinated in the nucleus by compounds such as iodine mono- and trichloride, ferric chloride, antimony pentachloride and molybdenum pentachloride, even in the absence of any free chlorine. The function of the chlorine in these processes appears to be, therefore, the constant regeneration of the original compound which effects the actual chlorination.

To account for the extraordinary influence of the conditions of halogenation on the type of substitution, a number of theories have been advanced. Bruner [1a] made the suggestion that side chain substitution is caused by interaction with molecular halogen and nuclear substitution results from the action of atomic halogen. On the other hand, Holleman [1b] believed that, whereas molecular halogen is responsible for side chain substitution, nuclear substitution occurs by interaction with a perhalide of the type HBr_x, a view also favored by Cohen.[1c] The view that nuclear substitution is caused by the action of ionized halogen atoms is now gaining favor. Schluederberg [2] pointed out that each of the halogen carriers mentioned above can dissociate with the production of negatively charged halogen atoms, thus:

$$ICl \longrightarrow I^+ + Cl^-$$

$$FeCl_3 \longrightarrow FeCl_2^+ + Cl^-$$

and hence he believed that nuclear chlorination of benzene is due to the action of negatively charged halogen. Schluederberg's theory also accounts for the nuclear substitution which occurs in the electrochemical chlorination of aromatic hydrocarbons since electrolytic chlorine may be considered to be negatively charged.

Directly opposed to the theory of Schluederberg is that of Fry,[3] who believed that nuclear substitution of aromatic hydrocarbons is effected by halogen atoms bearing a positive charge. The fact that the presence of moisture promotes nuclear substitution with toluene has been explained by Fry on the basis of his theory as follows: Chlorine first reacts with water to yield HCl and HOCl, and the latter then acts as a source of positive chlorine, HO^-Cl^+, which replaces a positive hydrogen in the ring.

THE CHLORINATION OF BENZENE

Chlorine can react with benzene in two entirely different ways, depending upon the conditions of chlorination. In the absence of the usual catalysts (halogen carriers) the photochemical reactions lead to a purely *addition* reaction with the formation of a hexachlorocyclohexane, according to the equation, $C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$. The direct addition reaction also takes place when chlorine is passed into boiling benzene in the absence of catalysts. Passage of ethylene into a mixture of benzene and chlorine, in the dark, results in the formation of hexachlorocyclohexane (of which the α-form melting at 157° C. predominates) together with some substitution products.[4] On the other hand, chlorination of benzene in the presence of practically all usual halogen carriers yields exclusively chlorine *substitution* derivatives of that hydrocarbon, irrespective of whether the process is carried out in light or at the boiling point of the hydrocarbon. The substitution reactions, which are far more important than the addition reaction, may be represented by the following series of stepwise equations:

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[1] Phosphorus halides appear to accelerate chlorination in aliphatic side-chains rather than in aromatic nuclei (see Erdmann, *Ann.*, 1893, 272, 148; *Chem. Soc. Abs.*, 1893, 64 (1), 160; Marckwald, U. S. Patent 721,961, Mar. 3, 1903; British Patent 17,695, 1902; *J.S.C.I.*, 1903, 22, 945).

[1a] Bruner and Dluska, *Bull. acad. sci. Cracow*, 1907, 693; *Chem. Soc. Abs.*, 1908, 94 (1), 146.

[1b] Holleman, Polak, van der Laan and Euwes, *Proc. K. Akad. Wetensch.* Amsterdam, 1905, 8, 512; *Rec. trav. chim.*, 1908, 27, 435; *cf.* Holleman, "Die direkte Einführung von Substituenten in der Benzolkern," Veit und Co., Leipzig, 1910, 83.

[1c] Cohen, Dawson, Blockey and Woodmansey, *J.C.S.*, 1910, 97, 1623; *cf.* Cohen, "Organic Chemistry for Advanced Students," Longmans, Green and Co., New York, 1913, 2, 397.

[2] *J. Phys. Chem.*, 1908, 12, 595.

[3] Fry, "Electronic Conception of Valence and the Constitution of Benzene," Longmans Green and Co., London, 1921. See also LeBas, *Phil. Mag.*, 1914, 27, 740; *Chem. Abs.*, 1914, 8, 3735; Fry, *J.A.C.S.*, 1916, 38, 1323; *ibid.*, 1917, 39, 1688.

$$\begin{aligned} C_6H_6 + Cl_2 &\longrightarrow C_6H_5Cl + HCl \\ C_6H_5Cl + Cl_2 &\longrightarrow C_6H_4Cl_2 + HCl \\ C_6H_4Cl_2 + Cl_2 &\longrightarrow C_6H_3Cl_3 + HCl \end{aligned}$$

By intensive chlorination in the presence of catalysts, tetra-, penta-, and hexachlorobenzenes may be obtained.

Although chlorine carriers accelerate the substitution reaction to the total exclusion of the addition reaction, the former can be accomplished without the aid of catalysts, i.e., by electrochemical chlorination or by chlorination at high temperatures in the vapor phase, both of which result in the formation of substitution products.

The chlorination of benzene can also be accomplished by subjecting that hydrocarbon to the action of certain substances capable of furnishing chlorine such as, for example, sulphuryl chloride, sulphur monochloride, or ferric chloride. All these reagents combine with benzene to yield substitution products exclusively.

Photochemical Chlorination. The velocity of the reactions of benzene with chlorine in the total absence of catalysts and in the dark is exceedingly small and, since traces of impurities or even the influence of the surface of the containing vessels may appreciably accelerate such reactions, exact measurements are difficult. According to Berthelot and Jungfleisch,[5] chlorine and benzene do not react in the dark to any appreciable extent below 300° C. A number of earlier workers obtained the lower melting form of 1,2,3,4,5,6-hexachlorocyclohexane by treatment of benzene with chlorine in direct sunlight at room temperature.[6] This hexachloro-derivative exists in two stereoisomeric forms, both of which are obtained by introducing chlorine into boiling benzene in the presence of light.[7] Although the direct addition of chlorine to benzene to yield hexachlorocyclohexane should proceed through the intermediate formation of a dichloride and a tetrachloride, these compounds have never been isolated from the reaction products, probably because they combine with chlorine at a much greater speed than does benzene itself.

The photochemical chlorination of benzene has been the subject of an intensive study by Luther and Goldberg,[8] who have shown that the reaction is powerfully inhibited by the presence of even a small amount of oxygen. Benzene free from dissolved oxygen was speedily chlorinated at ordinary temperatures when exposed to light from a "Uviol" lamp.[8a] The kinetics of the photochemical reaction between chlorine and benzene at 25° C. have been investigated by Slator,[9] who stressed the difficulty of removing the last traces of chlorine carriers from the sphere of reaction. In the absence of chlorine carriers the velocity of the photochemical reaction was found to be very small but Slator failed to realize the important inhibitory action of oxygen on this reaction.

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[4] Stewart and Hanson, *J.A.C.S.*, 1931, **53**, 1121.

[5] Quoted by Mounevrat and Pouret. *Compt. rend.*, 1898, **127**. 1025.

[6] Faraday, *Ann. chim.*, 1825, (2) **30**, 274; Mitscherlich, *Ann. Physik*, 1835, **35**, 370; Luther and Goldberg. *Z. physik. Chem.*, 1906. **56**. 43.

[7] Meunier, *Compt. rend.*, 1884, **98**, 436; *Chem. Soc. Abs.*, 1884, **46**, 733; Schüpphaus, *Ber.*, 1884, **17**, 2256. Luther and Goldberg. *loc. cit.*

[8] *Z. physik. Chem.*, 1906, **56**, 43; *Chem. Soc. Abs.*, 1906, **90** (2), 641. See also Goldberg, *Z. wiss. Photograph. Photophysik. Photochem.*, **4**, 61; *Chem. Soc. Abs.*, 1906, **90** (2), 513.

Catalytic Chlorination. A large amount of work has been carried out on the catalytic chlorination of benzene in the liquid phase. In the presence of a chlorine carrier, the absorption of chlorine is very rapid even at 0° C. and the products consist exclusively of substitution derivatives of benzene. The catalytic chlorination of benzene is now carried out on a large scale for the production of monochlorobenzene and iron is used as a catalyst. The chlorination process under these conditions is cumulative and if carried to completion yields hexachlorobenzene. Although iron is employed as a catalyst almost exclusively in the technical chlorination of benzene, laboratory experiments have shown that a large number of other substances are capable of exerting a powerful catalytic action on the reaction. Among these may be mentioned iodine, molybdenum pentachloride, vanadium tetrachloride, aluminum chloride, tin tetrachloride, thallic chloride, and amalgamated aluminum.

One of the earliest discovered catalysts for the substitutive chlorination of benzene was *elemental iodine*. By treating benzene in the cold with rather less than two atomic proportions of chlorine, Jungfleisch[10] obtained monochlorobenzene. Continued chlorination in the cold and in the presence of iodine and water furnished p-dichlorobenzene[11] as well as a little o-dichlorobenzene[12] but prolonged chlorination in the presence of iodine at elevated temperatures was found by Jungfleisch[13] to give rise to a mixture of higher chlorinated substitution products of benzene including 1,2,4-trichloro-, 1,2,4,5-tetrachloro-, pentachloro-, and hexachloro-benzenes.

The catalytic activity of molybdenum pentachloride on the chlorination of aromatic hydrocarbons was discovered by Aronheim,[14] who considered that this carrier was preferable to iodine since it acts very rapidly and uniformly and is more readily separated from the products of reaction. Thus anhydrous benzene, containing about 1 per cent of its weight of molybdenum pentachloride, when heated on the water bath completely absorbed a rapid stream of chlorine. On cooling the resulting liquid solidified to a crystalline mass which, after washing with ammonia, was found to consist mainly of p-dichlorobenzene with no monochlorobenzene or unchanged hydrocarbon.

In connection with the catalytic chlorination of benzene the early work of Willgerodt[15] is of importance. This investigator pointed out that the chlorination reaction was greatly accelerated by the presence of elements whose chlorides were readily capable of giving up part of their chlorine. Iron, antimony and tin were found to be active and also, to a less extent, bismuth, arsenic and amorphous phosphorus. Later[16] it was found that, although metallic indium did not at first accelerate chlorination, as soon as it was partly converted into its chloride an immediate catalytic influence was noted and the product then consisted mainly of p-dichlorobenzene. An immediate acceleration of the chlorination reaction occurred with metallic gallium and the products consisted of mono- and di-chlorobenzenes together with a little hexachlorocyclohexane. Willgerodt considered that the catalytic power of various elements in the chlorination of aromatic hydrocarbons was a function of their atomic weights (being greatest with elements of highest atomic weight), provided that the elements were capable of combining with chlorine. In a later publication Willgerodt[17] gave the results of a comprehensive investigation of the catalytic influence of various elements and their chlorides on the chlorination of benzene in the dark. The results are briefly summarized below, substitution products being formed in all cases.

[8a] The use of ultraviolet radiation in the halogenation of aromatic hydrocarbons was also discussed by Ellis and Wells, "The Chemical Action of Ultraviolet Rays," Chemical Catalog Co., Inc., New York, 1925, 195.

[9] *J.C.S.*, 1903, 83, 729.

[10] *Ann. chim.*, 1868 (4), 15, 252; also Müller, *Jahresber.*, 1862, 41.

[11] Müller, *Jahresber.*, 1864, 524; Jungfleisch, *loc. cit.*

[12] Beilstein and Kurbatow, *Ann.*, 1875, 146, 42; 1876, 182, 94.

[13] *Ann. chim.*, 1868, (4) 15, 264, 277, 283, 287.

[14] *Ber.*, 1875, 8, 1400.

[15] Willgerodt, *J. pr. Chem.*, 1885, (2), 31, 539.

[16] Willgerodt, *J. pr. Chem.*, 1887, (2) 35, 142; *Chem. Soc. Abs.*, 1887, 52, 326.

Zirconium	"very active"
Molybdenum	
Tellurium	
Iodine	
Columbium and its chlorides	active
Tantalum and its chlorides	
Uranium and its chlorides	
Lanthanum	slightly active
Vanadyl chloride	
Thorium and its chloride	almost inactive

The following elements, or their chlorides, were found to be *quite inactive:* yttrium and its chloride, titanium, germanium and its chloride, cerium and its chloride, didymium, chromic chloride, and sulphur monochloride.

The catalytic influence of thallic chloride on the substitutive chlorination of benzene has been noted by Thomas[18] and that of tin by Pétricou.[19] The chlorination of benzene in the presence of anhydrous aluminum chloride has been studied by Mouneyrat and Pouret,[20] who found that this compound exerts a great accelerating influence on the reaction. Chlorine was rapidly absorbed when passed into dry benzene, containing 3 per cent of aluminum chloride, at 50° to 55° C. When one molecular proportion of chlorine was absorbed, the products were found to consist of monochlorobenzene and a mixture of the three dichlorobenzenes together with some unreacted benzene. Further chlorination of benzene or of mono- or di-chlorobenzenes under similar conditions gave a mixture of higher chlorinated substitution products, in which three trichlorobenzenes, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene were found.

An investigation of the chlorination of aromatic compounds in the presence of the aluminum-mercury couple has been recorded by Cohen and Dakin.[21] On passing chlorine into 50 grams of anhydrous benzene containing 0.5 gram of the aluminum-mercury couple, the whole being cooled in ice, the benzene became first yellow, then rapidly turned dark violet and large quantities of hydrogen chloride were evolved, the couple remaining practically unattacked. The process was stopped when the benzene had increased in weight by 13 grams. Distillation of the products gave the following fractions:

Below 127° C.	4 grams
127° to 137° C.	50 grams
137° to 160° C.	5 grams
Above 160° C.	4 grams

The amount of crude monochlorobenzene corresponds to about 70 per cent of the theoretical yield while p-dichlorobenzene was isolated from the residue boiling above 160°. Cohen and Dakin also studied the chlorination of chlorobenzene in the presence of an aluminum-mercury couple. Chlorination of 10 grams of crude monochlorobenzene in 10 grams of carbon tetrachloride yielded 14 grams of product boiling at 130° to 230° C. and consisting of 1,2,4,5-tetrachlorobenzene together with some trichlorobenzene, probably the 1,2,4-compound. A theoretical yield of hexachlorobenzene was obtained by further chlorination of the tetrachlorobenzene in the presence of amalgamated aluminum.

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[17] *J. pr. Chem.*, 1887, (2) 35, 391.
[18] *Compt. rend.*, 1907, 144, 33.
[19] *Bull. soc. chim.*, 1890, (3) 3, 189.
[20] *Compt. rend.*, 1898, 127, 1025.
[21] *J.C.S.*, 1901, 79, 1111.

According to Lowy and Frank,[22] the chlorination of benzene to monochlorobenzene is accelerated by the presence of *water*.

As previously stated, in industrial practice iron is generally used as a catalyst for the chlorination of benzene to chlorobenzene. Mixtures of finely divided iron and ferric chloride have been stated to catalyze the reaction more completely than iron itself. In order to prevent the formation of dichlorobenzene, a deficiency of chlorine is usually employed (i.e., about 40 parts of chlorine are introduced per 78 parts of benzene instead of the theoretical 71 parts of chlorine, so that an excess of benzene remains unchanged after chlorination) and the temperature is not allowed to rise above a certain limit, which is usually considered to be about 40° C. In practice, about 60 per cent of the theoretical quantity of chlorobenzene can be obtained in one operation, the excess of benzene being recovered for re-chlorination. The results of three experiments[23] on the chlorination of benzene in the presence of 0.5 per cent of iron at a temperature not exceeding 40° C. are given in Table 125.

TABLE 125.—*Chlorination of Benzene in the Presence of Iron.*

	1	2	3
Benzene (parts by weight)	80	80	80
Increase in weight to	89	97	118
Fractionation of Products			
B.p. up to 100° C.	60	35	—
100° to 120° C.	6	25	—
120° to 140° C.	23	28	50
Above 140° C.	—	—	60
Residue	—	9	8
	89	97	118

Refractionation of the products of the second experiment yielded 35 parts of benzene, 10 parts of partially chlorinated benzene, 40 parts of chlorobenzene of boiling point 128° to 134° C., and 5 to 10 parts of dichlorobenzene. The third experiment furnished a considerable amount of dichlorobenzene.[24]

According to Bourion,[25] in the industrial chlorination of benzene in the presence of iron as a catalyst, the yield of monochloro-derivative increases with the velocity of chlorination but decreases slightly with rise in temperature. For a given concentration and a given temperature, the molar proportion of benzene converted into monochlorobenzene is about 8.5 greater than the molar proportion of benzene converted into p-dichlorobenzene.

Pyridine bases have also been used as halogen carriers in the chlorination of benzene. Cross and Cohen[26] obtained 30 parts of chlorobenzene together with some dichlorobenzene by bubbling chlorine through 50 parts of benzene at 50° C. containing a small proportion of pyridine. Similar results were obtained with other hydrocarbons (toluene and naphthalene), with another halogen (bromine), and with other bases (quinoline and isoquinoline).

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[22] *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 107; *Chem. Abs.*, 1923, **17**, 2086.

[23] Grandmougin, *Rev. prod. chim.*, 1917, **20**, 216.

[24] In connection with the use of iron in the chlorination of aromatic hydrocarbons, it is of interest to note that Fierz-David (*Naturwissenschaften*, 1929, **17**, 13; *Chem. Abs.*, 1929, **23**, 1886) observed that iron mixed with about 0.10% of iodine was a most powerful catalyst for chlorination reactions.

[25] *Compt. rend.*, 1920, **170**, 1319; *J.S.C.I.*, 1920, **39**, 480A.

[26] *Proc. Chem. Soc.*, 1908, **24**, 15; *Chem. Abs.*, 1908, **2**, 1450; *Chem. Zentr.*, 1908, **2**, 153.

It will be seen from the foregoing that the use of the majority of chlorine-carriers, which accelerate the chlorination of benzene, results in the production of substitution derivatives exclusively, the addition reaction being almost entirely suppressed even in bright sunlight. A few isolated statements appear to indicate, however, that not all catalysts induce substitutive chlorination but that on the contrary certain materials accelerate the addition reaction. Thus, Willgerodt[27] observed that in the presence of aluminum hydroxide or aluminum sulphate chlorination of benzene yielded mainly hexachlorocyclohexane. It has also been stated[28] that when a mixture of benzene and dry chlorine is passed in the vapor phase over a heated catalyst of partially reduced cupric chloride the products consist partly of the two isomeric hexachlorocyclohexanes together with some liquid products.

Electrolytic Chlorination of Benzene. The electrolytic chlorination of benzene dissolved in ether saturated with zinc chloride was studied by Schluederberg.[29] About 76 to 80 per cent of the chlorine was removed from inorganic combination. On the other hand, when benzene floating on a solution (160 grams of sodium chloride and 140 grams of sulphuric acid made up to 1 liter with water) was electrolyzed using a rotating anode, entirely immersed in the benzene layer, an efficiency of only 2.29 per cent was obtained. The necessity of employing a homogeneous solution was therefore clearly indicated. Schluederberg found that nascent chlorine produced during electrolysis yields substitution products with aromatic hydrocarbons and in this respect resembles chlorine in the presence of a halogen carrier rather than chlorine in the presence of chemically active radiation. To ensure homogeneity van Name and Maryott[30] used glacial acetic acid as a solvent for benzene and an electrolyzing agent of lithium chloride. On electrolysis of this solution chlorination was found to occur, but it also took place when chlorine was bubbled through the reaction mixture. They therefore concluded that the reaction between benzene and chlorine was catalyzed by the lithium chloride, and that chlorination took place due either to the chlorine liberated by electrolysis or simply bubbled into the solution, and not by anodic chlorination. One of the most exhaustive studies of the electrolytic chlorination of benzene has been made by Fichter and Glantzstein,[31] who electrolyzed a mixture of benzene and concentrated aqueous hydrochloric acid, rendered homogeneous by the addition of glacial acetic acid. A platinum anode was employed. Electrolysis of this solution gave under various conditions monochlorobenzene, p-dichlorobenzene, sym-tetrachlorobenzene and hexachlorobenzene. When the electrolysis was carried on for a long time, pentachlorophenol and chloroanil were also formed. The relative amounts of these substances present in the reaction product depended regularly upon the current density employed (other conditions being equal), indicating that an electrochemical reaction was taking place. The best yields were obtained with 3 faradays, i.e., a current yielding 3 gram-atoms of chlorine per mole of benzene. Increasing the concentration of the benzene up to the point where an emulsion was formed (nearly 1 mole per liter) improved the yield of chlorinated products. The most important factor in the course of the chlorination was current density. Thus, by raising the amperage up to about 1 ampere per sq. cm., the total yield was increased as well as that of the higher chlorinated products, while no hexachlorobenzene was formed at all with current densities less than 0.26 ampere per sq. cm. The best conditions for the production of higher chlorinated products, particularly hexachlorobenzene, were found to be low concentrations of benzene, high current densities and higher temperatures. The total yield and the yield of hexachlorobenzene were greater at platinum anodes than at graphite or magnetic iron oxide anodes, but in the presence of the last two substances oxidation reactions became more pronounced.

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[27] *J. pr. Chem.*, 1886, (2), **34**, 264.
[28] Tei and Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1927, **10A**, 325; *Chem. Abs.*, 1928, **22**, 1086.
[29] *J. Phys. Chem.*, 1908, **12**, 595.
[30] *Amer. J. Sci.*, 1913, **35**, 153; *Chem. Abs.*, 1913, **7**, 1444.
[31] *Ber.*, 1916, **49**, 2473.

A comparison of the electrolytic and chemical chlorinations of benzene has been made by Lowy and Frank,[32] who electrolyzed a well agitated mixture of 12 per cent aqueous hydrochloric acid (or a 20 per cent aqueous sodium chloride solution) and benzene, using a platinum anode. Under the conditions of agitation the mixture resembled an emulsion. The yield of monochlorobenzene was found to increase with rise in temperature up to 60° C. and to be affected by the rate of stirring. The introduction of iodine as a catalyst into the electrolytic bath increased the yield of chlorobenzene. On the other hand, the amount of higher chlorinated products as well as the amount of anodic oxidation of the benzene increased with rise of temperature. In comparative experiments on the electrolytic and purely chemical chlorination of benzene in the presence of 12 per cent aqueous hydrochloric acid, the same yield of chlorobenzene was obtained but the former method gave a small amount of higher chloro-derivatives, which were not furnished under conditions used by the purely chemical process.

Thermal Chlorination of Benzene. A study of the thermal chlorination of benzene at high temperatures in the vapor phase was made by Mason, Smale, Thompson and Wheeler.[33] Mixtures of chlorine and benzene vapor, containing an excess of the latter, were passed at high space velocities through silica reaction tubes heated over 30 cm. of their length to temperatures up to 600° C., and the products were analyzed by distillation methods. It was found that for a given space velocity there is a critical temperature below which the amount of chlorine unconsumed increases rapidly, but above a certain temperature pyrolysis sets in and carbon is deposited. When using unpacked silica tubes and a space velocity

TABLE 126.—*Thermal Chlorination of Benzene at Varying Space Velocities.*

Temperature 450° C. Molar ratio, $Cl_2:C_6H_6 = 1:22$; unpacked tube.

Tube Diameter Cm.	Space Velocity Min^{-1}	Benzene Converted into C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_3Cl_3$	Unchanged Cl_2; On Input
		Per Cent			
0.5	50	32.1	2.7	Nil	Nil *
0.5	100	28.2	4.3	Nil	6.2
0.5	250	22.5	2.2	3.1	20.8
1.0	20	34.6	3.6	Nil	Nil *
1.0	50	34.3	3.7	Nil	0.3
1.0	100	23.7	4.6	Nil	20.6
1.0	160	9.2	2.6	1.9	50.9
2.0	5	34.6	3.7	Nil	Nil *
2.0	10	34.5	3.2	Nil	Nil
2.0	15	35.9	2.7	Nil	Nil
2.0	25	34.0	4.2	Nil	1.1
2.0	50	30.2	3.1	.Nil	13.5
2.0	65	16.8	3.5	1.5	28.9

* Carbon deposited, owing to pyrolysis.

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[32] *Trans. Amer. Electrochem. Soc.*, 1923, 43, 107; *Chem. Abs.*, 1923, 17, 2086. See also Croco and Lowy, *Trans. Amer. Electrochem. Soc.*, 1926, 50, 315; *Chem. Abs.*, 1926, 20, 3396.

[33] *J.C.S.*, 1931, 3150.

of 50 reciprocal minutes[34] some pyrolysis occurred at temperatures of 500° C. and above, though pyrolysis was also observed at 450° C. when using lower space velocities, i.e., 5 reciprocal minutes. The effect of varying space velocity on the proportion of reaction products is shown in Table 126.

In Table 126 it is demonstrated that with each tube and above a certain space velocity the percentage of unreacted chlorine increases rapidly. When large amounts of unconsumed chlorine were found in the reaction products trichlorobenzene was found also.

The effect of varying the molecular ratio of chlorine to benzene in the thermal chlorination at 450° C. in a silica tube 1.0 cm. diameter, using a space velocity of 50 reciprocal minutes is shown in Table 127.

TABLE 127.—*Thermal Chlorination of Benzene with Varying Molecular Ratios of Chlorine to Benzene.*

Temperature 450° C.; unpacked tube; space velocity 50 min^{-1}.

Molar Ratio $Cl_2:C_6H_6$	Benzene Converted into C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_3Cl_3$	Unreacted Chlorine; on Input	Ratio $C_6H_5Cl:C_6H_4Cl_2$
	Per Cent				
1:1.1	44.7	15.2	Nil	Nil	2.9
1:1.6	43.3	6.8	Nil	0.3	6.4
1:2.2	34.3	3.7	Nil	0.3	9.3
1:3.4	24.0	2.2	Nil	0.5	10.9

It is evident that the production of dichlorobenzenes is depressed (relative to the monochlorobenzene) by an excess of benzene. There is an increased production of dichlorobenzenes without the formation of trichlorobenzene.

By packing the reaction tube with pieces of silica the speed of chlorination was increased but the reaction was not complete under these conditions at 375° C. with a space velocity of 10 reciprocal minutes. The influence of a number of volatile catalysts on the vapor phase chlorination was also studied and the results are shown in Table 128.

TABLE 128.—*Thermal Chlorination of Benzene with Various Catalysts.*

Tube diameter, 2.0 cm. Temperature, 450° C. Space velocity 50 reciprocal minutes: molar ratio, $Cl_2:C_6H_6 = 1:2.2$.

Catalysts and Wt. per Gm. Benzene	Benzene Converted to C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_3Cl_3$	Unreacted Cl_2 on Input
	Per Cent			
None	30.2	3.1	Nil	13.5
Iodine, 0.005 gm.	32.2	4.4	Nil	2.5
$AlCl_3$ (amount not estimated)	33.6	4.3	Nil	4.8
$FeCl_3$ (amount not estimated)	28.4	6.3	0.5	0.6

All these catalysts therefore accelerated the vapor phase chlorination especially ferric chloride, the use of which increased the production of dichlorobenzenes and also yielded some trichlorobenzene.

The vapor phase thermal chlorination of benzene is not as rapid as that of toluene. The results for both benzene and toluene are in excellent agreement (when only mono- and di-substitution products are formed) with the kinetic formula of Martin and Fuchs[85] for a bimolecular two-stage process. This is also demonstrated in Fig. 31, on page 773, in which the experimental values for the chlorination of toluene are very close to the theoretical curves.

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[34] Space velocity in reciprocal minutes has been defined by Mason, Smale, Thompson and Wheeler as the number of volumes of gas, at the reaction-tube temperature, passing through the heated zone per minute.

Chlorination of Benzene by Substances other than Chlorine. A number of chlorine-containing substances are capable of effecting the chlorination of benzene under the influence of heat. Among these may be mentioned the usual chlorine carriers such as iodine chlorides, ferric chloride, antimony pentachloride, and molybdenum pentachloride. Chlorination may also be effected by nascent chlorine generated from manganese dioxide and hydrochloric acid, while the chlorination of benzene at high temperatures in the presence of mixtures of hydrogen chloride and oxygen has also been accomplished.

The fact that benzene can be chlorinated by many of the usual chlorine carriers used as catalysts in the direct chlorination of such hydrocarbons lends strong support to the view that these carriers are active by virtue of their ability to supply chlorine in a more active condition than the ordinary molecular state. Thus Page[86] has found that molybdenum trichloride does not assist chlorination below the temperature (70° C.) at which it is converted by the action of chlorine into the pentachloride. The chlorination of a number of aromatic hydrocarbons by means of ferric chloride alone has been described by Thomas.[87] On heating benzene with ferric chloride, hydrogen chloride was evolved and the products contained monochlorobenzene, 1,4-dichloro-, 1,2,4-trichloro-, 1,2,4,5-tetrachloro-, pentachloro-, and hexachlorobenzenes. The production of hexachlorobenzene during the intensive chlorination of benzene by means of ferric chloride[88] and also antimony pentachloride[89] has been observed. Sulphur monochloride is said to chlorinate benzene to monochlorobenzene at 250° C.,[40] while monochlorobenzene is also formed by heating benzene with sulphuryl chloride to 160° C.[41] Seyewitz and Biot[42] obtained monochlorobenzene by heating benzene with ammonium lead tetrachloride ($2NH_4Cl.PbCl_4$) in a sealed tube at 150° C.

A very powerful chlorinating agent, capable of bringing about a high degree of chlorination of benzene and also of its homologues, consists of a solution of sulphur monochloride in excess sulphuryl chloride in the presence of aluminum chloride.[43] With the aid of this reagent, Silberrad has succeeded in obtaining a number of polychloro-derivatives of benzene and nuclear polychloro-derivatives of toluene.

Industrial Methods for the Chlorination of Benzene. Chlorination of benzene is carried out technically on a very large scale for the production of monochlorobenzene[43a] exclusively. This substance finds extensive application as an intermediate in the production of synthetic dyestuffs and also in the production of phenol. With the possible exception of p-dichlorobenzene, which is produced as an unavoidable by-product in the technical manufacture of the monochloro-derivative, none of the other chlorobenzenes has become of industrial importance. On a technical scale, the chlorination is carried out in the presence of an iron catalyst with cooling to prevent the temperature rising above a certain point, and the chlorination is usually stopped when less than 1 mole of chlorine per mole of

[85] *Z. Elektrochem.*, 1921, **27**, 150; see Chapter 29.

[86] *Ann.*, 1884, **225**, 196.

[87] *Compt. rend.*, 1898, **126**, 1211.

[88] Page, *Ann.*, 1884, **225**, 200.

[89] Muller, *Jahresbericht*, 1864, 523.

[40] Schmidt, *Ber.*, 1878, **11**, 1173.

[41] Dubois, *Z. für Chem.*, 1866, 708.

[42] *Compt. rend.*, 1902, **135**, 1120.

[43] Silberrad, *J.C.S.*, 1922, **121**, 1015.

[43a] The process used by the United Alkali Co., Ltd., for the manufacture of monochlorobenzene has been described (Anon., *Ind. Chem.*, 1925, **1**, 337; *Chem. Abs.*, 1925, **19**, 3148).

benzene has been absorbed in order to minimize the production of dichlorobenzene. A chlorination plant designed for this operation has been described by Marckwald.[44] In another similar process,[45] a mixture of ferric chloride and iron was proposed as a catalyst. The stream of chlorine is stopped before all the benzene is chlorinated and, at the end of the reaction, the contents are distilled under reduced pressure. The catalyst remains behind and can be used again, and the unreacted benzene is resubjected to chlorination. Thus, 156 kilos of chlorine were introduced into 300 kilos of benzene containing 1 kilo of ferric chloride and 1 kilo of powdered iron. On distillation, the product yielded 145 kilos of first runnings, containing a mixture of benzene and chlorobenzene which was subjected to further chlorination using 30 kilos of chlorine. The total yield from the initial 300 kilos of benzene was 335 kilos of pure monochlorobenzene and 24 kilos of p-dichlorobenzene, together with 13 kilos of mixed chlorinated benzenes.

Rabinovitz[46] chlorinated benzene in the presence of a special catalyst made by triturating in a mortar a mixture of equal weights of reduced iron powder and hydrated ferric chloride ($FeCl_3.6H_2O$). The resulting mass first liquefies and afterwards solidifies with evolution of heat and a sub-chloride is said to be formed. Chlorination of benzene is then carried out in the presence of 1 per cent by weight of the above catalyst at a temperature of 10°-15° C. with good agitation in a current of dry, air-free chlorine.

Coutagne[47] proposed to chlorinate benzene in the presence of iron at 15° C. in such a way that fresh chlorine comes in contact with fresh benzene. This is effected by allowing a stream of benzene to flow through a vertical series of basins exposed to a stream of dry chlorine also flowing in the same direction. The formation of higher chlorinated products is further reduced by admixture of hydrogen chloride with the chlorine.

In the continuous process of Auger[48] a stream of chlorine is totally absorbed in a controlled stream of liquid benzene (free from catalyst) in an absorption tower packed with siliceous pebbles. The solution of chlorine in benzene then passes to a cooled reaction chamber where it comes in contact with a catalyst of iron borings, whereupon reaction ensues and chlorobenzene and hydrogen chloride are produced. The hydrogen chloride passes off from the top of the reaction chamber while the chlorobenzene and unchanged benzene continuously overflow into a washer where neutralization is effected by means of moist chalk. The liquid mixture then passes through a container to a continuous still. It is estimated that the crude reaction product contains 30 per cent of monochlorobenzene and that the proportion of chlorobenzene to polychlorinated products is about 100:6. Auger's process is reported to have been used extensively in France and Italy.

Benzene may also be chlorinated by heating it with a mixture of manganese dioxide and hydrochloric acid to a temperature just below its boiling point.[49] Apparatus for the chlorination of benzene in the presence of an iron catalyst in the liquid phase has been described by Boulogne and Meillassoux,[50] and a method of recovering hydrogen chloride produced in the chlorination of benzene was described by Townsend.[51]

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[44] British Patent 17,695, 1902; *J.S.C.I.*, 1903, **22**, 945. German Patent 142,939, 1903; *Chem. Zentr.*, 1903, **2**, 609. U. S. Patent 721,961, March 3, 1903.

[45] Saccharinfabrik A.-G. vorm. Fahlberg, List und Co., German Patent 219,242, 1907; *J.S.C.I.*, 1910, **29**, 619; *Chem. Abs.*, 1910, **4**, 2186.

[46] U. S. Patent 1,189,736, July 4, 1916; assigned to Ellis-Foster Co.; *J.S.C.I.*, 1916, **35**, 885.

[47] French Patent 480,151, 1915; *J.S.C.I.*, 1917, **36**, 129.

[48] U. S. Patent 1,180,964, Apr. 25, 1916; and British Patent 100,105, 1916; *Chem. Abs.*, 1916, **10**, 1694. French Patent 482,372, 1917; *Chem. Abs.*, 1917, **11**, 3289.

[49] Soc. chim. usines du Rhône anciennement Gilliard, Monnet et Cartier, French Patent 479,645, 1914; *J.S.C.I.*, 1916, **35**, 1131.

[50] German Patent 382,048, 1922; *J.S.C.I.*, 1924, **43**, 88B.

It has been proposed to utilize hydrogen chloride as a source of chlorine for the chlorination of benzene at high temperatures in the vapor phase. A mixture of benzene vapor, hydrogen chloride, and oxygen, with or without the addition of other gaseous diluents, is passed at high temperatures over catalysts such as iron, thallium, alkaline earth or rare earth chlorides, or charcoal.[52] The reaction is said to take place also in the presence of catalysts consisting of copper with one or more elements of the 3rd or 8th Groups.[53]

The chlorination of benzene has been effected[54] at 300° C. or higher by the passage of a mixture of benzene vapor, hydrogen chloride vapor, steam and oxygen, or air, over a catalyst of pumice impregnated with copper chloride. Monochlorobenzene and other chlorinated hydrocarbons have been suggested as selective solvents for the purification of crude anthracene and similar substances by fractional sublimation.[54a]

Monochlorobenzene is a colorless liquid with a faint aromatic odor; boiling at 132° C. and having d^{20}_{4} 1.10601. It is used in the manufacture of sulphur black and other dyestuffs, and is finding increasing application as a raw material for the production of both phenol and aniline. Although the chlorine atoms in nuclear substituted aromatic chlorohydrocarbons are firmly bound and undergo reaction with much greater difficulty than in the case of similar aliphatic chlorohydrocarbons, the application of high pressure renders possible the hydrolysis of chlorobenzene to phenol. Thus Brown[55] described the Aylsworth process in which chlorobenzene and sodium hydroxide solution are continuously pumped under a pressure of 2500 to 3000 lbs. per square inch through a coil of hydraulic pipe immersed in a bath of molten sodium nitrite at 370° C. The resulting sodium phenoxide is discharged, condensed, acidified, and the liberated phenol distilled. Griswold[56] hydrolyzed chlorobenzene to phenol continuously by heating it with caustic soda at 350° C. under a pressure of 280 kg. per sq. cm. The hydrolysis of chlorobenzene with steam at high pressure according to the equation,

$$C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl,$$

has been described by Hale and Britton[57] and more phenol is now being manufactured in the United States by this method than by the old method of alkali fusion of benzenesulphonic acid.[58]

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[51] U. S. Patent 1,468,220, Sept. 18, 1923; assigned to Hooker Electrochemical Co.; *J.S.C.I.*, 1923, **42**, 1153A.

[52] E.g., Gremli, Austrian Patents 108,421 and 108,424, 1924; *Brit. Chem. Abs.* **B**, 1930, 50.

[53] Raschig G.m.b.H., French Patent 715,009, 1931; *Chem. Abs.*, 1932, **26**, 1625.

[54] British Patent 208,155, 1922; *J.S.C.I.*, 1924, **43**, 246B. Prahl (German Patent 539,176, 1930; assigned to F. Raschig G.m.b.H.; *Chem. Abs.*, 1932, **26**, 2989; *cf.* Prahl and Mathes, German Patent 575,765, 1933; assigned to F. Raschig G.m.b.H.; *Chem. Abs.*, 1933, **27**, 5082) used the same method for the preparation of other chlorinated isocyclic compounds in which all the hydrogen atoms are attached to the nucleus, for example, dichlorobenzene, dichlorodiphenyls and chloronaphthalenes.

[54a] Jaeger, British Patents 364,628 and 364,629, 1929; assigned to The Selden Co.; *Chem. Abs.*, 1933, **27**, 1642; *cf.* The Selden Co., British Patent 364,723, 1929; *Chem. Abs.*, 1933, **27**, 1643.

[55] *J. Ind. Eng. Chem.*, 1920, **12**, 279. Also Aylsworth, U. S. Patents 1,213,142 and 1,213,143, Jan. 23, 1917; *J.S.C.I.*, 1917, **36**, 382.

[56] U. S. Patent 1,833,485, Nov. 24, 1931; assigned to Dow Chemical Co.; *Chem. Abs.*, 1932, **26**, 1000. Also U. S. Patent 1,821,800, Sept. 1, 1931; *Chem. Abs.*, 1931, **25**, 5901. Britton (U. S. Patent 1,836,307, Dec. 15, 1931; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 220) obtains o- and p-hydroxydiphenyl (o- and p-phenylphenol) by distilling crude tar from the reaction of phenyl chloride and sodium hydroxide.

[57] *Ind. Eng. Chem.*, 1928, **20**, 114. See also Putnam, U. S. Patent 1,921,373, Aug. 8, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 5086. In a similar method (Raschig G.m.b.H., British Patent 387,832, 1932; *Brit. Chem. Abs.* **B**, 1933, 297) the phenol and hydrogen chloride are recovered (without condensing the excess chlorobenzene and steam) by washing with water and alkali. Britton and Perkins (U. S. Patent 1,862,075, June 7, 1932; assigned to Dow Chemical Co.; *Chem. Abs.*, 1932, **26**, 4068) use this method for the hydrolysis of chlorocyclohexane to ortho- and para-cyclohexylphenol.

[58] Frolich, *Ind. Eng. Chem.*, 1931, **23**, 111.

According to Ushakov and Zelinsky,[58a] cuprous and cupric oxides are better catalysts than copper for the preparation of phenol from chlorobenzene. In the presence of a melt containing 2.5 parts of cuprous oxide and 60 parts of copper, the hydrolysis proceeds at 260° to 280° C. At 320° C. a 95 per cent yield is obtained after 25 minutes. Addition of 30 per cent diphenyl to the monochlorobenzene reduces the quantity of sodium hydroxide required. In a similar way, aniline is now being manufactured by heating chlorobenzene with ammonia[59] under pressure in the presence of copper catalysts,[59a] the reaction being:

$$C_6H_5Cl + NH_3 \longrightarrow C_6H_5NH_2 + HCl$$

The product is said to be purer than that obtained from benzene by nitration and reduction.

Similarly, Hale[59b] suggested the reaction of chlorobenzene with sodium acid sulphide in the presence of 10 per cent of diphenyl sulphide and 3 per cent of diphenyl oxide for the manufacture of thiophenols.

Chalkley[59c] studied the vapor-phase hydrolysis of phenyl halides in a search for new methods for the synthesis of phenol. He found that phenyl chloride and bromide are hydrolyzed to the extent of at least 25 to 40 per cent by passing their vapors mixed with steam over silica gel at 500°-550° C. and atmospheric pressure. The reaction is catalyzed also by titania, alumina, thoria, zirconia, and blue tungsten oxide, of which silica gel and titania appear to be the most active. The products are the halogen acid, phenol and diphenyl oxide. The activity of the catalysts may be restored by heating in air or oxygen.

p-Dichlorobenzene is a crystalline solid with a faint odor, melting at 52.9° C. and boiling at 173° C.[59d] It has found some application as a moth- and insect-repellant. Kipriyanov and Daschevski[59e] observed that on hydrolysis with aqueous sodium hydroxide it gives a maximum of 30 per cent of p-chlorophenol. With sodium methoxide and some copper powder at 225° C., yields as high as 85 per cent result. Further hydrolysis to pyrocatechol can be affected by sodium hydroxide in the presence of copper sulphate provided a copper or silver-lined autoclave is employed.[59f] Similarly, p-dichlorobenzene reacts with aqueous ammonia in the presence of copper to give p-aminophenol.[59g] Kipriyanov and his associates[59h] described the preparation of chloronitrophenols, chloronitroanilines, chloroaminophenols, and chloroaminophenolsulphonic acids from p- and o-dichlorobenzene.

THE BROMINATION OF BENZENE

On account of the relatively greater cost compared with the corresponding chloro-derivatives the bromine substitution products of benzene are of little industrial significance. From a scientific point of view, the bromination reactions of benzene are closely similar to those of chlorination. The direct addition of six atoms of bromine to benzene with the production of the lower melting hexabromocyclohexane occurs in the presence of sunlight using dry reagents.[60] The same compound is also formed by the addition of bromine to an ice cold mixture of benzene and 1 per cent caustic soda solution.[61] By the action of bromine vapor on boiling benzene, Couper[62] obtained monobromobenzene and p-dibromobenzene. Excess bromine reacts with boiling benzene to form mainly p-dibromobenzene with only a small proportion of isomeric dibromo-derivatives.[63] As in the chlorination reaction, the bromination of benzene is greatly accelerated by the use of certain catalysts, among which may be mentioned iodine,[64] aluminum halides,[65] amalgamated aluminum,[66] ferric halides,[67] phosphorus halides, and antimony halides.[68] In the presence of these halogen carriers, bromination occurs with the production of monobromobenzene and also of higher bromine substitution products, the degree of bromination depending upon the amount of bromine used and upon the temperature. By the action of two moles of bromine on benzene in the presence of iodine, Jannasch[69] obtained mainly p-dibromobenzene. The same compound with only small amounts of isomers was obtained by Leroy[70] by the action of 960 grams of bromine on 240 grams of benzene in the presence of aluminum chloride. Of the other two dibromo isomers formed the m-dibromobenzene was found to be present in the largest quantity, being equivalent to about 10 per cent of the bromine consumed. It would appear, therefore, that when the reaction takes place in the presence of aluminum chloride there is a tendency for the formation of the para- and meta-derivatives. Larger proportions of bromine result in the formation of increasing amounts of polybromo-derivatives. Thus Scheufelen[71] produced a mixture of p-dibromo-, 1,2,4-tribromo-, and 1,2,4,5-tetrabromobenzenes by the addition of 3.5 moles of bromine to cooled benzene in the presence of ferric chloride as a catalyst. By dropping benzene into an excess of cooled bromine in the presence of the same catalyst Scheufelen obtained the fully brominated product, hexabromobenzene.

[58a] *J. Appl. Chem., Russia,* 1932, 5, 364; *Brit. Chem. Abs.* **A**, 1933, 267.

[59] Hale and Britton, U. S. Patent 1,607,824, Nov. 23, 1926; assigned to Dow Chemical Co.; *Chem. Abs.*, 1927, 21, 249. Williams (U. S. Patent 1,840,760, Jan. 12, 1932; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 220) suggested heating 1 mole of chlorobenzene with 1 mole of ammonia, 0.5 mole of slaked lime and 0.5 mole of calcium chloride in the presence of a cupric oxide catalyst at 175° C. under a pressure of 14 atmospheres, for the manufacture of aromatic ammonia compounds.

[59a] In order to obtain the full effect of the copper catalyst, the iron and steel apparatus can be rendered passive toward copper compounds by heating with aqueous ammonia to a temperature of 200° to 400° C. under superatmospheric pressure, according to Britton (U. S. Patent 1,921,726, Aug. 8, 1933; assigned to Dow Chemical Co.; *Chem. Abs.*, 1933, 27, 5082).

[59b] U. S. Patent 1,825,662, Oct. 6, 1931; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1933, 218.

[59c] *J.A.C.S.*, 1929, 51, 2489.

[59d] "International Critical Tables," McGraw-Hill Book Co., Inc., 1926.

[59e] *Ukrain. Khem. Zhur.*, 1932, 7, 78; *Brit. Chem. Abs.* **B**, 1933, 215; *Chem. Abs.*, 1933, 27, 3824.

[59f] Kipriyanov and Sytch, *Ukrain. Khem. Zhur.*, 1932, 7, 94; *Brit. Chem. Abs.* **B**, 1933, 215.

[59g] Kipriyanov, Kipriyanov and Daschevski, *Ukrain. Khem. Zhur.*, 1932, 7, 87; *Brit. Chem. Abs.* **B**, 1933, 215.

[59h] Kipriyanov and Mikhaïlenko, *Ukrain. Khem. Zhur.*, 1930, 5, 225; Kipriyanov and Daschevski, *ibid.*, 1930, 5, 241; *Chem. Abs.*, 1931, 25, 5033.

The dynamics of the bromination of benzene in the presence of various catalysts has been investigated by Bruner,[72] who found that the reaction was retarded by hydrogen bromide. In experiments in which iodine was used as a catalyst, the velocity constant of bromination was approximately proportional to the square of the iodine concentration.

The electrolytic bromination of benzene has been studied by Croco and Lowy,[73] who found that the only product formed was monobromobenzene.

The Chlorination of Toluene

In the direct chlorination of toluene, as well as of its homologues, two types of substitution take place, namely, (1) *nuclear chlorination*, in which chlorine atoms are substituted for hydrogen atoms in the aromatic ring, and (2) *side chain chlorination,* in which the aliphatic side chain undergoes substitutive chlorination. The extent to which these two types of substitution reactions proceed depends markedly upon the conditions of chlorination. Thus chlorination in the absence of halogen carriers, either with illumination in the cold or in the dark at the boiling point of the hydrocarbon, results preponderatingly in the formation of products containing the halogen in the side chain. On the other hand, the presence of practically all the usual halogen carriers[74] causes nuclear chlorination to occur, even in the presence of strong sunlight or at the boiling point of the hydrocarbon. In the electrolytic chlorination of toluene, nuclear substitution products are chiefly formed. Thermal chlorination of toluene at high temperatures in the vapor phase in the absence of specific halogen carriers causes the substitution of chlorine atoms in the side chain exclusively, but when the thermal reaction is carried out in the presence of volatile halogen carriers some nuclear chlorination also takes place.

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[60] Mitscherlich, *Ann. Physik*, 1835, **35**, *374*; for the action of bromine on an excess of benzene in sunlight see Collie and Frye, *J.C.S.*, 1898, **73**, 241.

[61] Orndorff and Howells, *Amer. Chem. J.*, 1896, **18**, 315; *cf.* Matthews, *J.C.S.*, 1898, **73**, 243.

[62] *Ann. chim.*, 1858, (3) **52**, 309; *Ann.*, 1857, **104**, 225.

[63] Riese, *Ann.*, 1872, **164**, 162, 176.

[64] Schramm, *Ber.*, 1885, **18**, 607.

[65] Leroy, *Bull. soc. chim.*, 1887, (2) **48**, 211, 213; *Chem. Soc. Abs.*, 1888, **54**, 258.

[66] Cohen and Dakin, *J.C.S.*, 1899, **75**, 894.

[67] Scheufelen, *Ann.*, 1885, **231**, 187, 189; *Chem. Soc. Abs.*, 1886, **50**, 340.

[68] Bruner, *Bull. Acad. Sci. Cracow*, 1901, 22; *Chem. Soc. Abs.*, 1901, **80** (2), 441.

[69] *Ber.*, 1877, **10**, 1355.

[70] *Bull. soc. chim.*, 1887, (2) **48**, 211, 213.

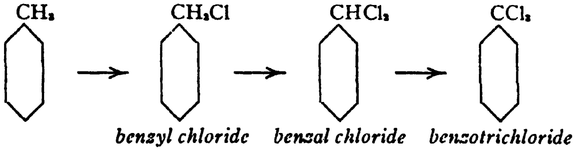
[71] *Ann.*, 1885, **231**, 187, 189; *Chem. Soc. Abs.*, 1886, **50**, 340.

[72] *Z. physik. Chem.*, 1902, **41**, 513; *cf.* the results of Slator (*J.C.S.*, 1903, **83**, *729*) on the dynamics of the chlorination of benzene in the presence of iodine as a cataylst.

[73] *Trans. Amer. Electrochem. Soc.*, 1926, **50**, 315; *Chem. Abs.*, 1926, **20**, 3396.

The addition reaction, which has been observed for benzene, has only been noted in a few instances with toluene, and appears to be quite unknown with higher homologues. Pieper[75] noted the separation of crystals of octachloromethylcyclohexane, $C_7H_6Cl_8$, melting at 150° C., from a solution of chlorine in toluene. Additive compounds of chlorine and toluene have also been reported by Qvist,[76] who obtained compounds from which about 50 per cent of the chlorine content could be eliminated in the form of hydrogen chloride by alcoholic potash with the production of di- and tri-chlorotoluenes.

Direct Chlorination in Absence of Catalysts and Illumination. The products of the direct (very slow) chlorination of toluene at room temperature in the dark or in diffused daylight are mainly nuclear substituted derivatives. According to Schramm,[77] o- and p-chlorotoluenes are produced under these conditions, but Limpricht[78] obtained a mixture of both nuclear and side chain substituted products. In direct sunlight, however, substitution occurs predominantly in the side chain even at room temperature. By introducing chlorine into boiling toluene, even in the dark, side chain substitution occurs almost exclusively and the products are benzyl chloride,[79] benzal chloride,[80] and benzotrichloride,[81] depending upon the extent of chlorination. The progressive chlorination of toluene at the boiling point in the absence of halogen carriers can therefore be represented as follows:



Book and Eggert[82] reported that the chlorination of toluene at 105° to 110° C. with a stream of chlorine of definite velocity yields the same products irrespective of whether the reaction takes place in the dark or in the presence of illumination. In the absence of chlorine carriers the product is benzyl chloride, but in the presence of ferric chloride, o- and p-chlorotoluenes are formed.

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[74] Phosphorus trichloride appears to be an exception to this rule since, as previously mentioned, it catalyzes side chain substitution.

[75] Pieper, *Ann.*, 1867, **142**, 304; *cf.* Cohen and Dakin, *J.C.S.*, 1904, **85**, 1279.

[76] *Finska Kemistsamfundets Medd.*, 1928, **37**, 45; *Chem. Abs.*, 1929, **23**, 117.

[77] *Ber.*, 1884, **17**, 2922; 1885, **18**, 350, 606, 1272; 1886, **19**, 212.

[78] *Ann.*, 1866, **139**, 304; *cf.* Beilstein and Geitner, *Ann.*, 1866, **139**, 332.

[79] Cannizzaro, *Ann. chim.*, 1855, (3) **45**, 468; *Compt. rend.*, 1855, **41**, 517.

[80] Beilstein and Geitner, *Ann.*, 1866, **139**, 332.

[81] Beilstein and Kuhlberg, *Ann.*, 1868, **146**, 322, 331.

[82] *Z. Elektrochem.*, 1923, **29**, 521; *Chem. Abs.*, 1924, **18**, 668; *Ber.*, 1926; **59**, 1192.

Both benzyl chloride and benzal chloride are of industrial importance and their production is carried out on a large scale by chlorinating toluene at its boiling point. Phosphorus trichloride is used as a catalyst in this process [83] and unlike other chlorine carriers it does not appear to induce nuclear substitution.

Photochemical Chlorination in Absence of Catalysts. In general, chemically active light radiation, such as sunlight or the light of a mercury vapor lamp, accelerates the chlorination of toluene at low temperatures and in the absence of the usual halogen carriers promotes substitution in the side chain. Schramm [84] found that the chlorination of toluene in the cold in direct sunlight resulted in the production of benzyl chloride, benzal chloride, and benzotrichloride without formation of nuclear substitution products. Schramm considered that the yellow and green rays were the most active in promoting this chlorination but the use of light from a mercury vapor lamp has been advocated in several instances. The results of Book and Eggert [85] showed that, though the purely chemical (dark) reaction of chlorine on toluene ceases at temperatures of the order of —80° C. and no reaction can be observed after 70 hours, combination can be initiated even at this low temperature under the influence of illumination from a mercury vapor lamp. On the other hand, the purely chemical reaction at 105° to 110° C. so predominates over the photochemical process that the influence of the latter is obscured at this higher temperature.[86] At room temperature, however, the reaction between chlorine and toluene is undoubtedly accelerated by illumination.[86a]

As with benzene, the photochemical chlorination of both toluene and xylene in acetic acid solution is retarded by the presence of oxygen.[87]

Catalytic Chlorination. Practically all the usual halogen carriers accelerate the chlorination of toluene and yield nuclear substitution products exclusively, with the exception of phosphorus trichloride. In the presence of 0.06 per cent of iodine, for example, chlorination of toluene takes place even at very low temperature (—80° C.).[88] By introducing a current of chlorine into toluene in the presence of iodine, no benzyl chloride is formed even at the boiling point, the products consisting of p-chlorotoluene [89] with some o-chlorotoluene [90] as well as nuclear polysubstitution products such as 2,4,5-trichlorotoluene.[91] Beilstein and Kuhlberg [92] obtained tetra- and penta-chlorotoluenes, consisting entirely of nuclear substituted derivatives, by chlorination in the presence of iodine followed by rechlorination of the product, boiling above 240° C., in the presence of antimony pentachloride.

Among the catalysts which have been found to accelerate the nuclear chlorination of toluene, the following may be specially mentioned: molybdenum pentachloride, sublimed ferric chloride, and aluminum amalgam. By passing dry chlorine into anhydrous toluene containing molybdenum pentachloride, Aronheim and Dietrich [93] obtained p-chlorotoluene as well as di- and tri-chlorotoluenes in which substitution had taken place exclusively in the nucleus. Seelig [94] studied the chlorination of toluene in the presence of this catalyst and also ferric chloride, and obtained o- and p-chlorotoluenes (the former predominating), 2,3- and 2,4-dichlorotoluenes, as well as trichlorotoluenes.

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[83] See, for example, Marckwald, British Patent 17,695, 1902; French Patent 328,053, 1902; German Patent 142,939, 1903; U. S. Patent 721,961, March 3, 1903.

[84] *Ber.*, 1885, **18**, 608.

[85] *Z. Elektrochem.*, 1923, **29**, 521; *Chem. Abs.*, 1924, **18**, 668; *Ber.*, 1926, **59**, 1192; *Chem. Abs.*, 1926, **20**, 2990.

[86] *Cf.* Bergel, *Ber.*, 1926, **59B**, 153; *Chem. Abs.*, 1926, **20**, 1602.

[86a] The effect of ultraviolet radiation on the chlorination of toluene was demonstrated by Ellis (Ellis and Wells, "The Chemical Action of Ultraviolet Rays," Chemical Catalog Co., Inc., New York, 1925, 213) by comparing the yields of products obtained on passing mixtures of toluene vapor and chlorine through a quartz tube both with and without exposure to ultraviolet light.

[87] Goldberg, *Z. wiss. Photographie, Photophysik u. Photochemie*, 1906, **4**, 61; *Chem. Zentr.*, 1906, **1**, 1693. Luther and Goldberg, *Z. physik. Chem.*, 1906, **56**, 43.

[88] Book and Eggert, *Z. Elektrochem.*, 1923, **19**, 521.

[89] Beilstein and Geitner, *Ann.*, 1866, **139**, 334.

[90] Hübner and Majert, *Ber.*, 1873, **6**, 790.

[91] Beilstein and Kuhlberg, *Ann.*, 1868, **146**, 318, 325.

[92] *Ann.*, 1869, **150**, 287, 298.

Cohen and Dakin [95] chlorinated toluene in the presence of an aluminum-mercury couple in the cold and obtained nuclear substituted derivatives exclusively. Thus, chlorination of 62 grams of dry toluene in the presence of the couple until an increase of 19.5 grams was obtained yielded the following fractions on distillation:

Below 140° C.	1.5 grams
140° to 163° C.	68.7 grams
Above 163° C.	2 grams

The yield of crude monochlorotoluene was about 80 per cent and this product was shown by oxidation to chlorobenzoic acids to consist of a mixture of about 65 per cent o-chlorotoluene and about 35 per cent of para-compound. By chlorination of toluene in the presence of the aluminum-mercury couple, so that larger proportions of chlorine were absorbed, Cohen and Dakin obtained good yields of dichlorotoluenes and trichlorotoluenes.

Lead chloride has also been shown to promote nuclear substitution of toluene. Thus, chlorination of toluene at 100° C. in the presence of lead chloride yielded a mixture of o- and p-chlorotoluenes containing about 62 per cent of the ortho isomer.[96] Selenium also catalyzes the nuclear substitution of chlorine atoms.[97]

Moisture promotes substitution of toluene in the ring, anhydrous halogens in the absence of carriers tending to substitute in the side chain.[98] Cohen, Dawson, Blockey, and Woodmansey [99] showed that although the chlorination of toluene in light by dry chlorine yields on the average 94 per cent of benzyl chloride and side chain substitution products, *moist* chlorine in the dark chlorinates *boiling* toluene with the formation of nuclear substitution derivatives to the extent of nearly 90 per cent. It thus appears definitely established that side chain substitution is favored by light, higher temperatures, and absence of moisture.

An apparent exception to the rule that halogen carriers promote nuclear substitution is phosphorus chlorides, which have been said to accelerate substitution in the side chain. Thus, Erdmann [100] observed that phosphorus pentachloride accelerated the chlorination of toluene in the side chain but not in the nucleus. This statement has been contested by Bergel,[101] but, on the other hand, Colson and Gautier [102] showed that benzal chloride is formed by heating toluene with phosphorus pentachloride in a sealed tube at 190° to 195° C. Moreover, in view of the fact that phosphorus trichloride has been repeatedly used as a catalyst for the production of benzyl and benzal chlorides by chlorination of boiling toluene,[103] it cannot be doubted that phosphorus chlorides differ markedly from other halogen carriers in their influence on the chlorination of benzene homologues. Another possible exception to the usual behavior of halogen carriers is sulphur, which is stated by Haeussermann and Beck[104] to promote side chain substitution in the chlorination of nitrotoluene.

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[93] *Ber.*, 1875, **8**, 1401.

[94] *Ann.*, 1887, **237**, 130, 131.

[95] *J.C.S.*, 1901, **79**, 1119.

[96] Wahl, Normand and Vermeylen, *Compt. rend.*, 1922, **174**, 946.

[97] Silberrad and Silberrad, *J.C.S.*, 1925, **127**, 2449.

[98] The theoretical implications of these and similar facts have been considered by Fry, "Electronic Conception of Valence."

[99] *J.C.S.*, 1910, **97**, 1623; also Cohen and Dutt, *J.C.S.*, 1914, **105**, 501; Cohen and Dakin, *J.C.S.*, 1906, **89**, 1453.

[100] *Ann.*, 1893, **272**, 150.

[101] *Ber.*, 1926, **59B**, 153.

[102] *Ann. chim.*, 1887, (6) **11**, 21.

[103] Marckwald, British Patent 17,695, 1902; Ellis, U. S. Patent 1,146,132, July 13, 1915, assigned to Chadeloid Chemical Co.; E. I. duPont de Nemours and Co., British Patent 879, 1913; Gibbs and Geiger, U. S. Patent 1,246,739, Nov. 13, 1917; Grandmougin, *Rev. prod. chim.*, 1917, **20**, 296.

Thermal Chlorination of Toluene. The thermal vapor phase chlorination of toluene was investigated by Ellis,[105] who showed that, in the absence of specific halogen carriers, chlorine enters the side chain exclusively. More recently these results have been extended by the work of Mason, Smale, Thompson and Wheeler.[106] These investigators studied the chlorination of toluene in the vapor phase at temperatures up to 700° C. in fireclay or silica tubes of various sizes. As the technical object desired was the complete utilization of the chlorine, an excess of toluene was usually employed. At temperatures above 600° C. pyrolysis of the products occurred even when using space velocities high enough to give no unchanged chlorine in the exit gas, i.e., with space velocities up to 3000 reciprocal minutes. In the temperature range 400° to 600° C., mixtures containing more than 1 volume of chlorine to 2 volumes of toluene could not be used owing to inflammation. Typical results of experiments at various temperatures in a fireclay tube 0.5 cm. in diameter are given in Table 129, and the experimental results were compared with theoretical figures calculated from the kinetic formula of Martin and Fuchs[107] for a bimolecular stepwise reaction (see Fig. 31).

TABLE 129.—*Thermal Vapor-Phase Chlorination of Toluene.*
Molecular ratio, chlorine : toluene = 1 :2.2

Temp. ° C.	Space Velocity Min.$^{-1}$	Toluene Converted into: Benzylchloride Obs.	Benzylchloride Calc.	Benzal Chloride Obs.	Benzal Chloride Calc.	Chlorine Recovered as Cl_2	HCl
		Per Cent					
400	500	—	—	—	—	23.1	—
500	500	30.5	30.0	2.3	4.6	Nil	56.2
600	500	20.1	19.9	1.6	1.7	Nil	64.1
600	1000	27.1	26.7	5.6	3.5	0.9	51.1
700	3000	22.3	24.2	4.6	2.7	0.9	59.1

In order to determine the speed of the vapor phase reaction at lower temperatures a fireclay tube of 2.3 cm. diameter was used and the results obtained are given in Table 130. These experimental results were also compared with those calculated from the formula of Martin and Fuchs (see Fig. 31).

TABLE 130.—*Thermal Vapor-Phase Chlorination of Toluene.*
Fireclay tube, 2.3 cm. diameter.

Mol. Ratio Cl_2:C_7H_8	Temp. ° C.	Space Velocity (Actual) Min.$^{-1}$	Toluene Converted into: Benzyl Chloride Obs.	Benzyl Chloride Calc.	Benzal Chloride Obs.	Benzal Chloride Calc.	Unchanged Cl_2; on Input
			Per Cent				
1:1.2	310	2.7	38.7	39.3	10.8	10.3	0.1
1:1.2	315	2.7	37.2	39.5	11.2	10.5	Nil
1:1.2	250	2.7*	32.5	38.0	10.4	9.1	0.6†
1:1.2	315	28.3*	30.4	31.9	6.9	5.4	Nil†
1.3:1	300	6.9*	43.5	44.4	26.3	21.8	0.7†

* Packed tube, containing fireclay packing of particles passing through 10 mm. and retained by 3 mm. sieve. Ratio of free space to total volume packed = 0.53.
† Much pyrolysis in these experiments.

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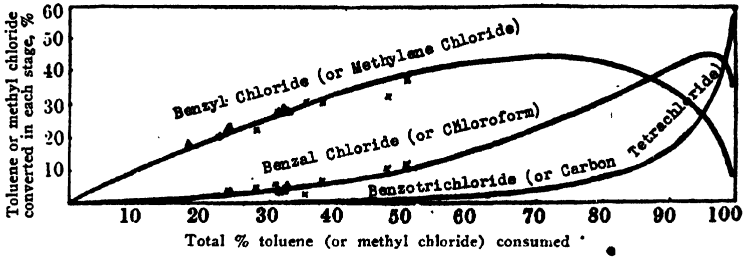
[104] *Ber.*, 1892, 25, 2445.

[105] Ellis, U. S. Patent 1,202,040, Oct. 24, 1916; assigned to Chadeloid Chemical Co.; *J.S.C.I.*, 1916, 35, 1212.

[106] *J.C.S.*, 1931, 3150.

[107] *Z. Elektrochem.*, 1921, 27, 150.

It will be seen that with an unpacked tube and a space velocity of 2.7 reciprocal minutes complete reaction was not obtained below 310° C. An increase in the proportion of chlorine resulted in the production of more benzal chloride. On the other hand, with a packed tube practically complete reaction could be obtained at 250° C. but the tendency to pyrolysis was enhanced.



Courtesy Journal of the Chemical Society

FIG. 31.—Non-Catalytic Vapor-Phase Chlorination of Toluene and Methyl Chloride. (Mason, Smale, Thompson and Wheeler.)

Continuous curves = theoretical curves for three-stage reaction
Points marked x = experimental values, chlorination of toluene
Points marked Δ = experimental values, chlorination of methyl chloride

The effect of the addition of volatile catalysts in the vapor phase chlorination of toluene at 500° C. in a fireclay tube of 0.5 cm. bore was also examined by Mason and his co-workers, whose results are shown in Table 131.

TABLE 131.—*Catalytic Vapor-Phase Chlorination of Toluene.*
Tube diameter, 0.5 cm. Temperature 500° C. Space velocity 500 min.$^{-1}$
Molar ratio, $Cl_2:C_7H_8 = 1:2.2$

	Toluene Converted into		
Catalyst	Benzyl Chloride	Benzal Chloride	Chloro-toluenes
	Per Cent		
None	30.5	2.3	Nil
Iodine (1% on toluene)	12.0	4.0	16.9
NH_3 (1% on toluene)	18.9	6.1	9.5
$CHCl_3$ (1% on toluene)	28.4	4.8	Nil
$FeCl_3$ Amount not estimated; qualitative only.	6.7	8.9	14.5
Sulphur	22.1	3.9	3.9
H_2O	29.0	4.4	Nil

The above results show that iodine, ferric chloride, ammonia and sulphur promote chlorination in the nucleus, but the addition of chloroform and water vapors tend only to increase the proportion of benzal chloride.

Electrochemical Chlorination of Toluene. Electrolytic chlorination of toluene has been shown to result almost exclusively in the production of nuclear substitution products. Mülhofer[108] obtained a good current yield of chlorotoluenes (30 per cent ortho-, and 70 per cent para-isomer) by electrolyzing a well-stirred mixture of 20 grams of toluene and 250 cc. of concentrated aqueous hydrochloric acid. No benzyl chloride was formed and the addition of iodine did not influence the nature or yield of the products. Schluederberg[109] found that in the electrolytic chlorination of toluene 76 to 96 per cent of the chlorine acting substituted in the ring and the rest in the side chain. Similarly, Cohen, Dawson and Crosland[110] electrolyzed toluene over a layer of concentrated hydrochloric acid with a carbon anode and found that substitution occurred mainly in the nucleus. When chlorine was bubbled through the same mixture under similar conditions substitution occurred almost entirely in the side chain, so that a true electrochemical reaction is to be presumed.

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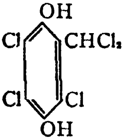
[108] Dissertation, "Über die Einwirkung elektrolytisch erzeugter Halogene auf organischen Verbindungen," Munich, 1905.

Fichter and Glantzstein[111] studied the electrolytic chlorination of toluene in the presence of concentrated (aqueous) hydrochloric acid using a platinum anode. The bath was rendered homogeneous by the addition of sufficient glacial acetic acid. The complexity of the product obtained from toluene and the difficulty of isolating individual compounds, hindered the systematic study of the reactions involved, but the important discovery was made that in the dark at least three chlorine atoms are introduced into the nucleus before the methyl group begins to undergo chlorination. Fichter and Glantzstein believed this to be good evidence in favor of Bruner's theory that atomic halogen attacks the nucleus and that side chains are chlorinated by molecular chlorine. The compounds identified, either by isolation or by an examination of their hydrolytic products, were: o- and p-chlorotoluenes, 2,4-dichlorotoluene, 2,4,5-trichlorotoluene, pentachlorotoluene, hexachlorobenzene, pentachlorobenzyl chloride, 2,4,5-trichlorobenzylidene dichloride, and also the compound



With a current density of 0.005 ampere per sq. cm., mono- and di-chlorotoluenes are the only products; at 0.01 ampere per sq. cm., trichlorotoluene makes its appearance; but the substituted quinol, which renders so difficult the identification of the products, is not formed until a current density of at least 0.05 ampere per sq. cm. is attained.

Chlorination of Toluenes by Substances other than Chlorine. By heating toluene with many of the usual halogen carriers (except phosphorus pentachloride) nuclear substitution products are formed exclusively.[112] Thomas[113] obtained nuclear substitution products only with no benzyl chloride by boiling toluene with anhydrous ferric chloride, and Seyewetz and Biot[114] produced o-chlorotoluene by heating toluene with the double compound of ammonium chloride and lead tetrachloride ($2NH_4Cl.PbCl_4$). Tertiary butyl hypochlorite chlorinates toluene in the side chain to benzyl chloride.[115]

Perhaps the most important chlorinating agent of this class is sulphuryl chloride, which has been applied in the technical manufacture of benzyl chloride from toluene. Wöhl's[116] process consists in treating an excess of toluene with sulphuryl chloride in the dark at a temperature not exceeding 110° C. when benzyl chloride is produced almost exclusively. Thus, a mixture of 200 kilos of toluene and 180 kilos of sulphuryl chloride is gently heated under reflux to about 103° C., the temperature being maintained below 110° C. until the evolution of hydrogen chloride ceases. On fractionally distilling the mixture somewhat more than half the toluene is recovered unchanged and an almost theoretical yield of benzyl chloride is obtained (calculated on the toluene reacting).

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[109] *J. Phys. Chem.*, 1908, **12**, 595.
[110] *J.C.S.*, 1905, **87**, 1034.
[111] *Ber.*, 1916, **49**, 2473; *Chem. Abs.*, 1917, **11**, 2667.
[112] Colson and Gautier, *Ann. chim.*, 1887, (6) 11, 21; *Chem. Zentr.*, 1887, 690.
[113] *Compt. rend.*, 1898, **126**, 1213.
[114] *Compt. rend.*, 1902, **135**, 1121.
[115] Clark, *Chem. News*, 1931, **143**, 265; *Chem. Zentr.*, 1932, 1, 1359.
[116] German Patent 139,552, 1901; *Chem. Zentr.*, 1903, 1, 607; German Patent 146,796, 1902; *Chem. Zentr.*, 1903, **2**, 1299; German Patent 160,102, 1902; *Chem. Zentr.*, 1905, **2**, 367; German Patent 162,394, 1930; *Chem. Zentr.*, 1905, **2**, 727.

Apparently sulphuryl chloride at higher temperatures tends to promote ring substitution, for Töhl and Eberhard[117] found that by heating toluene with sulphuryl chloride at 160° C. about one-third is converted into benzyl chloride and the residual two-thirds into p-chloro- and 3,4-dichlorotoluenes. The production of benzyl chloride was not reduced under these conditions by the addition of iodine though it was increased by exposure to light.

A very complete examination of the influence of a large number of catalysts on the course of the chlorination of toluene by means of sulphuryl chloride has been made by Silberrad, Silberrad and Parke.[118] Toluene was boiled with a 10 per cent excess of sulphuryl chloride (on an equimolar basis) for 8 hours in the presence of various catalysts and the products examined. Two types of catalysts were found, namely, (1) those that either exhibit chlorination or alter its course without accelerating it appreciably, and (2) those that accelerate substitution. Of the nineteen catalysts investigated, only phosphorus pentachloride, manganese chloride, and arsenic (in this order) were of the first class, inhibiting ring substitution and increasing the production of benzyl chloride. All the other catalysts (namely, auric chloride, aluminum chloride, carbon, stannic chloride, bismuth, antimony, sulphur monochloride, selenium, tellurium, chlorine, bromine, iodine, iron and platinum) accelerated ring substitution and, with the exception of sulphur and bromine, at the expense of benzyl chloride. Further, the catalytic activity of the elements (except bromine) was a function of their atomic weight, increasing with this property to a maximum. The elements of the same group showed a decreasing tendency to induce side chain substitution with increasing atomic weight.

It has been shown by Silberrad[119] that the efficacy of sulphuryl chloride as a nuclear chlorinating agent in the presence of aluminum chloride is greatly increased by the presence of sulphur monochloride. This combination is a very powerful chlorinating agent and is capable of bringing about the production of polychloro-derivatives very readily. By treating toluene (184 grams) in the presence of anhydrous aluminum chloride (10 grams) at 70° C. with varying amounts of the chlorinating agent (sulphuryl chloride + 1% sulphur monochloride), various nuclear polychloro-derivatives, including pentachlorotoluene, were obtained by Silberrad.[120]

Hypochlorous acid reacts with toluene to form either nuclear or side chain substitution products.[121] The following conditions favor nuclear substitution: absence of light, dilute (up to 1.0 N) solutions of hypochlorous acid, the use of solutions of hypochlorites and weak acids, such as boric and carbonic, and the presence of iron or copper salts. The most favorable conditions for side chain substitution are light rich in infra-red rays, temperatures higher than 40° C., and solutions of hypochlorites and strong acids.

[117] *Ber.*, 1893, **26**, 2940.
[118] *J.C.S.*, 1925, **127**, 1724; *Chem. Abs.*, 1925, **19**, 3197.
[119] *J.C.S.*, 1922, **121**, 1015.
[120] *J.C.S.*, 1925, **127**, 2677.
[121] Clark, *Chem. News*, 1931, **143**, 265; *Chem. Abs.*, 1932, **26**, 1591.

Industrial Applications of the Chlorination of Toluene. In the various processes which have been developed for the industrial chlorination of toluene, the production of side chain substituted products, principally benzyl and benzal chlorides, has been exclusively sought. Both benzyl and benzal chlorides are employed in the manufacture of benzaldehyde and benzoic acid, which find extensive application in the organic chemical industries.

Marckwald[122] produced benzyl and benzal chlorides by chlorination of hot liquid toluene by a stream of chlorine at a temperature just below the boiling point of toluene and in the presence of about 1 per cent of phosphorus trichloride, which acts as a catalyst for side chain substitution. In order to avoid the production of higher chlorinated products, apparatus is used in which the chloro-compound as produced is removed continuously from the action of the chlorine.

A continuous process of producing benzyl chloride was described by Ellis[123] in which a vaporized mixture of toluene, phosphorus trichloride, and chlorine (containing sufficient chlorine to convert 25 to 50 per cent of the toluene to benzyl chloride) is heated to 180° to 220° C. and exposed to ultraviolet light. The benzyl chloride is condensed and the mixture of toluene and phosphorus trichloride mixed with further quantities of chlorine and toluene and again subjected to the same process. Ellis[124] also proposed a thermal process in which a mixture of toluene vapor and sufficient chlorine to combine with 25 to 50 per cent of the toluene present is passed through a heated zone where it is subjected to a gradually increasing temperature above the boiling point of toluene. The benzyl chloride formed is condensed and the residual toluene, after being freed from hydrogen chloride, is again subjected to a similar thermal chlorination.

Gibbs and Geiger[125] produced side chain substituted toluene derivatives by exposing a heated mixture of toluene containing the theoretical amount of chlorine for the desired stage of chlorination to the action of ultraviolet radiation. The process is carried out at a temperature not materially below 150° C., and by using a "low pressure" mercury vapor lamp benzyl and benzal chlorides are formed, while by employing a "high pressure" lamp and three molecular proportions of chlorine, benzotrichloride is the chief product.[126] Benzyl chloride and bromide may be produced by the action of the corresponding halogen on toluene in the presence of chlorates.[127] The thermal vapor phase chlorination of toluene to yield benzyl chloride has been utilized by Mason and Wheeler.[128] The side chain chlorination of benzene homologues by vapor phase operation in the presence of illumination has been described by Conklin.[129]

Wohl's[130] process for the production of benzyl chloride by heating toluene with sulphuryl chloride under reflux at 103° to 110° C. has already been mentioned. The production of benzyl chloride by treatment of a mixture of toluene and bleaching powder with sulphur dioxide has been described by Conant.[131]

An interesting process for the production of benzyl chloride and its homologues is by condensation of benzene hydrocarbons with monochloroacetone in the presence of tin tetrachloride.[132] The process is exemplified by the production of p-methylbenzyl chloride by treatment of an equimolecular mixture of toluene and chloroacetone, dissolved in twice its weight of carbon disulphide or carbon tetrachloride and cooled to —10° C., with about one-fourth molecular proportion of tin tetrachloride, which is added drop by drop. The reaction product is poured onto ice and distilled to furnish a 60 per cent yield of p-methylbenzyl chloride.

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[122] British Patent 17,695, 1902; French Patent 328,053, 1902; German Patent 142,939, 1903; U. S. Patent 721,961, March 3, 1903.

[123] U. S. Patent 1,146,142, July 13, 1915; assigned to Chadeloid Chemical Co.; *J.S.C.I.*, 1915, **34**, 899. Canadian Patent 170,942; *Chem. Abs.*, 1918, **12**, 41.

[124] U. S. Patent 1,202,040, Oct. 24, 1916; assigned to Chadeloid Chemical Co.; *J.S.C.I.*, 1916, **35**, 1212.

[125] U. S. Patent 1,246,739, Nov. 13, 1917; assigned to Selden Co.; *J.S.C.I.*, 1918, **37**, 52A. See also Gibbs, Canadian Patent 186,446, 1918; *Chem. Abs.*, 1918, **12**, 2325.

[126] Gibbs, British Patent 123,341, 1917; assigned to Selden Co.; *J.S.C.I.*, 1919, **38**, 268A.

[127] Soc. chim. usines du Rhône anciennement Gilliard, Monnet et Cartier, French Patent 483,622, 1917; *Chem. Abs.*, 1918, **12**, 910.

[128] British Patent 342,329, 1919; assigned to Imperial Chemical Industries, Ltd.

[129] U. S. Patents 1,828,868 and 1,828,859, Oct. 27, 1931; assigned to Solvay Processes Co.; *Chem. Abs.*, 1932, **26**, 632.

[130] German Patent 139,552, 1903; *Chem. Zentr.*, 1903, **1**, 607; German Patents 160,102 and 162,394, 1905; *Chem. Zentr.*, 1055, **2**, 367, 727.

[131] U. S. Patent 1,233,986, July 17, 1917; *Chem. Abs.*, 1917, **11**, 2580.

Sors[132a] described apparatus for the manufacture of benzyl chloride by chlorination of toluene at its boiling point, and its subsequent hydrolysis with aqueous sodium carbonate solution to benzyl alcohol. Lead, glass, or stoneware are said to be satisfactory materials for construction of plant, but iron must be carefully avoided or coated completely with lead.

THE BROMINATION OF TOLUENE

Though the bromination reactions of the benzenoid hydrocarbons are as yet of little industrial importance, the influence of various factors on the course of the bromination of toluene has been investigated much more completely than the chlorination reactions of that hydrocarbon so that a brief account of the bromination of toluene is desirable if only because of the light that it sheds on the course of halogenation in general.

In the absence of catalysts, bromine reacts slowly with cooled toluene in the dark with the initial production of o- and p-bromotoluenes.[133] Under similar conditions but in *diffused daylight* nuclear chlorination is also accompanied by the formation of some benzyl bromide,[134] while in *direct sunlight* in the cold and in the absence of catalysts benzyl bromide is formed to the total exclusion of bromotoluenes.[135] The photochemical process therefore induces side-chain substitution even at low temperatures.

The influence of temperature alone in the distribution of substitution is very marked, low temperatures favoring nuclear substitution and higher temperatures bromination of the side chain. Thus the vapor phase bromination of toluene at temperatures above the boiling point yields benzyl bromide almost exclusively even in the dark.[136] Holleman and van der Laan[137] investigated the influence of temperature in the dark on the relative proportions of side chain and nuclear substitution. Table 132 shows the results on the bromination of toluene (50 cc.) with bromine (3 cc.) in the dark.

TABLE 132.—*Influence of Temperature on the Dark Bromination of Toluene.*

Temperature	Products		
	Benzyl Bromide	o-Bromotoluene	p-Bromotoluene
° C.	Per Cent		
25	10.6	35.5	53.9
50	43.7	23.5	32.8
75	86.3	6.2	7.5
100	100	—	—

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[132] French Patent 464,645, 1913; *J.S.C.I.*, 1914, **35**, 503. Also British Patent 30,068, 1913; *J.S.C.I.*, 1914, **33**, 668.

[132a] *Chem.-Ztg.*, 1933, **57**, 321; *British Chem. Abs.* **B**, 1933, 457.

[133] Glinzer and Fittig, *Ann.*, 1865, **136**, 301; Hübner and Wallach, *Z. für Chemie*, 1869, 138; *Ann.*, 1870, **154**, 294; Hübner and Post, *Ann.*, 1873, **169**, 5, 31, 159; Jannasch and Hübner, *Ann.*, 1873, **170**, 117; Schramm, *Ber.*, 1885, **18**, 606.

[134] Seelig, *J. pr. Chem.*, 1889, (2) **39**, 179.

[135] Schramm, *Ber.*, 1885, **18**, 606.

[136] Lauth and Grimaux, *Bull. soc. chim.*, 1867, (2) **7**, 109.

[137] *Proc. König. Akad. Wetensch. Amsterdam*, 1905, **8**, 512; *Chem. Soc. Abs.*, 1906, **90** (1), 154. Holleman, Polak, van der Laan and Euwes, *Rec. trav. chim.*, 1908, **27**, 435; *Chem. Soc. Abs.*, 1909, **96** (1), 93.

It was found also that side chain substitution was so greatly accelerated by light that benzyl bromide becomes the main product of bromination in diffused daylight even at as low a temperature as 25° C. The influence of light is therefore much more pronounced than that of heat in promoting substitution in the side chain. In addition the results appeared to indicate that molecular bromine acted only on the side chain, and complex bromides, of the type represented by HBr_x, attacked the nucleus.[138]

Factors which exert a very important directive influence on the course of the dark bromination of toluene are concentration of bromine, and the nature of the medium. Thus with diminishing concentration of bromine the substitution in the side chain tends to increase.[139] The influence of the addition of certain solvents to the bromination mixture has also been investigated[140] and it has been shown that the influence of such solvents not only manifests itself in the dark but also in the photochemical reaction. Dilution with nitrobenzene, and to a lesser degree with acetic acid and benzonitrile, results in an increase of the relative proportion of nuclear substitution. Dilution with carbon tetrachloride gives a substitution distribution ratio similar to that obtained by dilution with the same amount of toluene.

As in the case of the chlorination process, the usual halogen carrier catalysts accelerate nuclear substitution so powerfully as to overrule all other influences. Thus bromination of toluene in the presence of iodine as catalyst produces o- and p-chlorotoluenes and no benzyl bromide either at the boiling point of the hydrocarbon[141] or in the presence of direct sunlight.[142] Fine iron powder, even in so small a concentration as 0.002 mole ferric bromide per mole of bromine, inhibits the formation of benzyl bromide in the bromination of 50 cc. of toluene by 2.5 cc. of bromine in light at 50° C.[143] Antimony pentachloride and especially aluminum bromide, or amalgamated aluminum[144] also exert a powerful accelerating influence on nuclear substitution. Nuclear bromination may be carried to the limit by employing excess of bromine in the presence of these catalysts. For example, Gustavson[145] obtained pentabromotoluene, $C_6Br_5CH_3$, by dropping toluene into excess of bromine containing a little anhydrous aluminum bromide.

According to van der Laan,[146] phosphorus pentabromide is very sharply differentiated from the other halogen carriers in that it increases the yield of benzyl bromide without influencing the relative proportions of o- and p-bromotoluenes. The remarkable action of phosphorus halides in promoting substitution of halogens in the side chains of benzene homologues has already been mentioned.

THE CHLORINATION OF THE HOMOLOGUES OF TOLUENE

As with toluene, the halogenation reactions of its homologues can occur in two ways, either by substitution in the nucleus or by substitution in the side chain or chains. In general, nuclear chlorination of the higher alkylbenzenes is favored by low temperatures and the absence of light and especially by the presence of the usual halogen carriers. On the other hand, chlorination in the presence of sunlight or other chemically active radiation, as well as chlorination at the boiling point of the hydrocarbon, results mainly in substitution in the side chains.

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[138] Bruner and Dluska (*Bull. acad. sci. Cracow,* 1907, 691; *Chem. Soc. Abs.*, 1908, 94 (1), 146) and Bancroft (*J. Phys. Chem.*, 1908, 12, 439; *Chem. Abs.*, 1908, 2, 3027) have suggested that molecular bromide attacks the side chain while bromine ions attack the nucleus.

[139] Bruner and Dluska, *loc. cit.* Holleman, *et al.*, *loc. cit.*

[140] Bruner and Dluska, *loc. cit.*; Bruner and Vorbrodt, *Bull. acad. sci. Cracow,* 1909, 221; *Chem. Abs.*, 1910, 4, 3067.

[141] Beilstein, *Ann.*, 1867, 143, 370.

[142] Schramm, *Ber.*, 1885, 18, 606.

[143] Van der Laan, *Rec. trav. chim.*, 1907, 26, 39, 45.

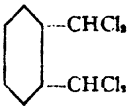
[144] Van der Laan, *Rec. trav. chim.*, 1907, 26, 43.

[145] *J. Russ. Phys.-Chem. Soc.*, 1877, 9, 216, 286; *Ber.*, 1877, 10, 971, 1183.

[146] *Rec. trav. chim.*, 1907, 26, 47.

Chlorination of toluene homologues in the dark in the absence of catalysts in the cold yields mainly nuclear substitution products. Thus, under these conditions mesitylene was found by Fittig and Hoogewerff[147] to form mono-, di-, and trichloro-derivatives, and pseudocumene gave 5-chloro- and 3,5,6-trichloro-1,2,4-trimethylbenzenes.[148]

Chlorination of benzene homologues at high temperatures, e.g., at the boiling points of the hydrocarbons, in the absence of halogen carriers and with or without illumination, forms substitution products with the chlorine atoms in the side chains. In this way, the corresponding xylyl chlorides and xylylene dichlorides have been prepared from ortho-,[149] meta-[149a] and para-xylenes.[150] In the presence of an excess of chlorine and at 140° C. two hydrogen atoms are substituted in each of the two side chains of o-xylene with the production of tetrachloro-o-xylene[151] of the formula



By treating 200 grams of boiling m-xylene in a quartz vessel exposed to light from mercury vapor lamps with a stream of chlorine until 64.8 grams of chlorine had been absorbed, Posner and Schreiber[152] obtained, after fractionation of the products, 183 grams of m-xylyl chloride and 41 grams of m-xylylene dichloride, of the formula $C_6H_4(CH_2Cl)_2$. Stine[153] has described the chlorination of p-xylene in sunlight at 100° C. to yield p-xylylene dichloride, which is then hydrolyzed and nitrated to furnish various explosive substances. It is interesting to note that nuclear chlorinated xylenes may also be further chlorinated in the side chains by photochemical chlorination at 120° C. In this way trichloro-m-xylene yields di(dichloromethyl)-trichlorobenzene.[154]

The products of the chlorination of some of the higher benzene homologues at their boiling points (and usually in daylight) in the absence of catalysts are given in Table 133.

TABLE 133.—*Products of Chlorination of Higher Benzene Homologues.*

Hydrocarbon	Formula of Product
Ethylbenzene[155]	$C_6H_5CH_2CH_2Cl$ and $C_6H_5CHClCH_3$
n-Propylbenzene[156]	$C_6H_5CH_2CHClCH_3$ and $C_6H_5CH_2CH_2CH_2Cl$
Mesitylene[157]	$(CH_3)_2C_6H_3CH_2Cl$ and $CH_3C_6H_3(CH_2Cl)_2$

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[147] *Ann.*, 1869, **150**, 323.

[148] Schultz, *Ber.*, 1909, **42**, 3604.

[149] Rayman, *Bull. soc. chim.*, 1876, (2) **26**, 534.

[149a] Vollrath, *Z. für Chem.*, 1886, 489. Lauth and Grimaux, *Bull. soc. chim.*, 1867, (2) **7**, 233; Gundelach, *Bull. soc. chim.*, 1876, (2) **26**, 43.

[150] Grimaux, *Compt. rend.*, 1870, **70**, 1364; *Ann.*, 1870, **155**, 340.

[151] Hjelt, *Ber.*, 1885, **18**, 2879.

[152] *Ber.*, 1924, **57B**, 1127; *Chem. Abs.*, 1924, **18**, 3368.

[153] U. S. Patent 1,309,551, July 8, 1919; *J.S.C.I.*, 1919, **38**, 659A.

[154] Schmidlin and Fischer, U. S. Patent 1,219,166, March 13, 1917; *J.S.C.I.*, 1917, **36**, 500; *Chem. Abs.*, 1917, **11**, 1557; Cassella and Co., British Patent 114,645, 1917; *J.S.C.I.*, 1918, **37**, 296A.

[155] Schramm, *Monatsh.*, 1887, **8**, 104; *Ber.*, 1893, **26**, 1707. Fischer and Schmitz, *Ber.*, 1906, **39**, 2209. Fittig and Kiesow, *Ann.*, 1870, **156**, 246. Hass (private communication) reports the formation of 8-9 per cent of β-chloroethylbenzene when chlorinating at room temperature in the presence of light.

[156] Errera, *Gaz.*, 1884, **14**, 506. Genvresse, *Bull. soc. chim.*, 1893, (3) **9**, 220. Errera apparently considered the product obtained on the chlorination of propyl benzene to be the β-derivative; Genvresse, however, showed that this product consisted of both the α- and β-derivatives.

[157] Robinet, *Compt. rend.*, 1883, **96**, 501; *Ber.*, 1883, **16**, 965. Colson, *Bull. soc. chim.*, 1883, (2) **40**, 110.

The photochemical chlorination of the higher alkylbenzenes in the absence of catalysts leads to the production of side-chain substituted derivatives almost exclusively even in the cold. Thus o-, m-, and p-xylenes yield the corresponding xylyl chlorides and xylylene dichlorides under these conditions, and m-xylene also gives some chloro-m-xylene.[158] Ethylbenzene in the cold in the presence of sunlight absorbs 1 mole of chlorine to form α-chloroethylbenzene[159] but further chlorination produces α,α-dichloroethylbenzene together with some nuclear substituted products.[160]

As in the case of toluene, chlorination of the higher alkylbenzenes in the presence of the usual halogen carriers leads predominantly to the formation of nuclear substituted derivatives even in the presence of sunlight or at the boiling point of the hydrocarbon. Nuclear substitution has been effected by many investigators by using iodine as a catalyst in the cold.[161] Iron has also been used.[162]

Nuclear substitution products are also obtained by heating the alkylbenzenes with the usual chlorinating agents in the absence of chlorine. Thus sulphuryl chloride chlorinates ethylbenzene in the nucleus in the presence of aluminum chloride to yield 4-chloro-1-ethylbenzene besides other products.[163] m-Xylene reacts with sulphuryl chloride at 160° C. to yield 4-chloro-m-xylene. In the presence of aluminum chloride 1,3-dimethyl-4-sulphonyl chloride is formed. By heating p-xylene with the double salt $2NH_4Cl . PbCl_4$, Seyewetz and Biot[164] obtained 2-chloro-p-xylene. An important exception to the general rule is phosphorus pentachloride. Thus, Colson and Gautier[165] found that by heating phosphorus pentachloride with o-, m-, and p-xylenes at 190° C. products were obtained containing up to four chlorine atoms substituted in the side chains.

THE BROMINATION OF THE HOMOLOGUES OF TOLUENE

Although a good deal of work has been carried out on the bromination of the higher benzene homologues a detailed discussion of the results cannot be given here. In brief, however, it may be said that the influence of various factors on the relative distribution of substitution in the nucleus and side chains respectively is almost identical with that observed in chlorination reactions. Diffused or direct sunlight and temperatures around the boiling point of the hydrocarbon promote substitution in the side chain and darkness and low temperatures yield nuclear substituted derivatives. The influence of catalysts such as iodine, or aluminum halides, is to promote substitution in the nucleus exclusively even under conditions which normally favor side chain substitution.

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[158] Radziewanowski and Schramm, *Bull. acad. sci. Cracow*, 1898, 61; *Chem. Zentr.*, 1898, **1**, 1019.

[159] Schramm, *Monatsh.*, 1887, **8**, 102.

[160] Radziewanowski and Schramm, *loc. cit.*

[161] *o-Xylene:* Kruger, *Ber.*, 1885, **18**, 1755; Claus and Bayer, *Ann.*, 1893, **274**, 305; Claus and Kautz, *Ber.*, 1885, **18**, 1368; Ferrand, *Compt. rend.*, 1901, **133**, 169; Villiger, *Ber.*, 1909, **42**, 3533. *m-Xylene:* Vollrath, *Ann.*, 1867, **144**, 266; Jacobsen, *Ber.*, 1885, **18**, 1761; Koch, *Ber.*, 1890, **23**, 2319; Hollemann, *Ann.*, 1867, **144**, 265; Claus and Burstert, *J. pr. Chem.*, 1890, (2) **41**, 556. *p-Xylene:* Kluge, *Ber.*, 1885, **18**, 2099; Willgerodt and Wolfien, *J. pr. Chem.*, 1889, (2) **39**, 402. *p-Ethyltoluene:* Defren, *Ber.*, 1895, **28**, 2648. *Pseudocumene:* Krafft and Merz., *Ber.*, 1875, **8**, 1302.

[162] *m-Xylene:* Claus and Burstert, *J. pr. Chem.*, 1890, (2) **41**, 553. *p-Xylene:* Rupp, *Ber.*, 1896, **29**, 1628.

[163] Töhl and Eberhard, *Ber.*, 1893, **26**, 2940. Töhl, *Ber.*, 1893, **26**, 2949.

[164] *Compt. rend.*, 1902, **135**, 1121.

[165] *Compt. rend.*, 1885, **101**, 1064; *Chem. Soc. Abs.*, 1886, **50**, 231; *Compt. rend.*, 1886, **102**, 689; *Chem. Soc. Abs.*, 1886, **50**, 613; *Ann. chim.*, 1885, (6) **6**, 109; *ibid.*, 1887, (6) **11**, 22; *Bull. soc. chim.*, 1886, (2) **45**, 509.

Chapter 33

Production of Alcohols by Hydrolysis of Alkyl Halides
Production of Esters

The alkyl halides, particularly the chlorides which may be manufactured relatively cheaply by direct chlorination of paraffin hydrocarbons, are possible raw materials for the production of monohydric alcohols of the aliphatic series. Not only secondary and tertiary alcohols but also primary ones, including ethanol and methanol, may be made by the hydrolysis of the appropriate alkyl chloride. This mode of synthesis of alcohols is therefore sharply differentiated from that involving the hydration of olefins which yields, except in the single instance of ethanol, secondary or tertiary alcohols only and cannot be used to make the simplest member, methanol.

The hydrolysis of alkyl chlorides to alcohols has usually been effected by treatment in the liquid phase with alkalies such as aqueous caustic soda, milk of lime or aqueous sodium carbonate, or in the gaseous phase by passing vaporized chloride over solid alkaline reagents or reagents capable of combining with, and fixing, hydrogen chloride. The reaction may be simply expressed as follows:

$$\underset{\textit{alkyl chloride}}{C_nH_{2n+1}Cl + M^IOH} \longrightarrow \underset{\textit{alcohol}}{M^ICl + C_nH_{2n+1}OH}$$

where M^I represents one atomic proportion of a monovalent element (or one-half atomic proportion of a divalent element).

The direct saponification of alkyl chlorides by steam in the vapor phase is known to proceed according to the reversible equation:

$$C_nH_{2n+1}Cl + H_2O \rightleftharpoons C_nH_{2n+1}OH + HCl,$$

but unfortunately, in general, the point of equilibrium even at elevated temperatures and in the presence of a large excess of steam appears to be well over toward the left. Accordingly, this method is of little value in the production of alcohols from alkyl chlorides but the reverse procedure may be employed successfully in many cases for producing alkyl halides from alcohols.

In the saponification of alkyl chlorides by alkalies to yield alcohols, it is necessary to control the conditions of the reaction, more especially the concentration of alkali and temperature, to minimize undesirable side reactions such as the elimination of hydrogen chloride to yield olefins according to the equation:

$$C_nH_{2n+1}Cl \longrightarrow C_nH_{2n} + HCl\ (\text{fixed})$$

Aliphatic ethers may also be produced by saponification under certain conditions.

Esters of aliphatic alcohols are obtained by heating alkyl halides with salts of the appropriate organic acids, the alkali or alkaline earth metal salts being most frequently employed. The reaction is exemplified by the conversion of amyl chloride into amyl acetate by heating with sodium acetate, thus:

$$C_5H_{11}Cl + NaOOCCH_3 \longrightarrow NaCl + C_5H_{11}OOCCH_3$$

The Conversion of Methyl Chloride into Methanol

Hydrolysis with Steam. The direct reaction of methyl chloride with steam in the vapor phase according to the equation:

$$CH_3Cl + H_2O \rightleftharpoons CH_3OH + HCl - 12 \text{ Cal.},$$

is a reversible process taking place with considerable heat absorption. Accordingly elevated temperatures should favor the hydrolytic process. Even at 350° C. and over in the presence of a large excess of steam the amount of methanol in equilibrium appears to be negligibly small. Application of the Nernst "approximation formula" to this equilibrium leads to a value for the equilibrium constant, $K_p = \frac{[CH_3OH]\,[HCl]}{[CH_3Cl]\,[H_2O]}$ of only about $2x10^{-4}$, at 350° C., showing that only relatively small amounts of methanol can be obtained even under equilibrium conditions. These theoretical considerations are completely substantiated by experimental results. For example Whiston[1] attempted to induce hydrolysis of methyl chloride with steam but found that only traces of methanol were produced. McKee and Burke[2] passed a mixture of steam and methyl chloride, in molar ratios varying from 1:1 to over 3:1 over a catalyst of pure silica at temperatures up to 350° C. but only traces of methanol and hydrogen chloride could be found in the products of reaction. Several other catalysts, including zirconium dioxide, anhydrous calcium chloride, anhydrous aluminum chloride and silica, were also tried but in every case only negligible quantities of methanol were produced.

Hydrolysis by means of Metallic Hydroxides. The reaction between alkyl halides and metallic hydroxides may be carried out either in the liquid phase using a solvent (in the case of methyl chloride this method of operation also involves the employment of pressure) or by passing the vapors of the alkyl halide over the heated solid hydroxides and condensing the alcohols so formed. The latter mode of procedure was employed by Dumas and Stas[3] in an attempt to produce methylene. By passing methyl chloride over hot potash lime, these investigators obtained potassium formate, potassium chloride, hydrogen and some methane. Similar results were obtained with solid sodium hydroxide and it was shown that the production of formates was due to the oxidation of the methanol initially formed.

Whiston[4] found that by repeated circulation of methyl chloride (without addition of steam) over calcium hydroxide at 300° C. the methyl chloride disappeared almost quantitatively. Although no experimental details or quantitative data were reported by Whiston, the presence of methanol and dimethyl ether was qualitatively demonstrated. An experimental and theoretical examination of the production of methanol by the passage of methyl chloride over heated metallic hydroxides was conducted by McKee and Burke.[5] Highly porous granular calcium hydroxide was an excellent material for effecting this reaction, but aluminum hydroxide proved unsatisfactory. On passing methyl chloride mixed with steam over granular calcium hydroxide at about 350° C. the methanol production was very high during the first few hours of the experiment. After a time, however, the reaction diminished due to the conversion of the surface layers of calcium hydroxide into calcium chloride, and eventually attained a low, but steady, value. The products of the reaction were mainly calcium chloride, methanol and dimethyl ether. The reactions involved together with the approximate thermal values are given in the following equations:

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[1] *J.C.S.*, 1920, 117, 183.

[2] *Ind. Eng. Chem.*, 1923, 15, 682.

[3] *Ann.*, 1840, 35, 169; *Ann. chim. phys.*, 1840, (2), 73, 157; *J. pr. Chem.*, 1840, (1), 21, 377; see Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1852, 7, 288.

[4] *J.C.S.*, 1920, 117, 183.

[5] *Ind. Eng. Chem.*, 1923, 15, 682, 788.

$$2CH_3Cl + Ca(OH)_2 = CaCl_2 + 2CH_3OH + 3 \text{ Cals.}$$
$$2CH_3Cl + 2CH_3OH + Ca(OH)_2 = CaCl_2 + 2CH_3OCH_3 + 2H_2O + 9 \text{ Cal.}$$

The optimum temperature for this process was 350° C. By using fairly high rates of flow, thermal decomposition of the reacting gases may probably be reduced to under 2 per cent while the methyl chloride can be almost quantitatively converted into methanol and methyl ether. The relative amounts of the two products depend upon the relative partial pressures of methyl chloride and steam in the reacting gases.

Using equal partial pressures of methyl chloride and steam, yields of methanol and methyl ether in the ratio of 67 to 33 were obtained. This ratio is, however, increased in favor of methanol by the use of higher partial pressures of steam. If, for example, the partial pressures of steam and methyl chloride are in the ratio of 3:1, the resulting ratio of methanol to ether is 80:20, approximately. The use of a large excess of steam has the disadvantage that it reduces the percentage utilization of the calcium hydroxide. An endeavor was therefore made to effect the catalytic conversion of the dimethyl ether into methanol separately. This hydration process, namely, $(CH_3)_2O + H_2O \rightleftarrows 2CH_3OH - 3$ Cal., is a reversible reaction catalyzed by aluminum oxide at temperatures in the region of 350° C. McKee and Burke found that in order to convert 50 per cent of dimethyl ether into methanol in the presence of this catalyst at 350° C. about 8.5 volumes of steam per volume of ether are necessary in the reacting gases. Less steam is required, however, if the hydration is carried out in a number of successive stages. By heating gaseous methyl chloride in the presence of a dilute solution of caustic potash in a sealed tube at 100° C. for one week, Berthelot[6] obtained some methanol. Under these conditions, however, the hydrolysis was exceedingly slow.

Industrial Processes. Lacy[7] reported a method of hydrolyzing alkyl halides, and particularly methyl chloride, which consists in heating the halide in intimate contact with an alkaline solution to temperatures considerably above 100° C. and at a pressure above the vapor pressure of the alkaline solution. For example, a pressure vessel of 9 liters capacity, furnished with stirring devices, is half filled with milk of lime containing 15 per cent by weight of calcium hydroxide and heated to 190° C. (equivalent to 167 lbs. pressure). Methyl chloride is then introduced until the pressure attains about 260 lbs. per square inch and this pressure is maintained by regulating the supply of methyl chloride. After 15 minutes the reaction mixture is said to contain 7 per cent of methanol which can be removed by distillation. A similar process involving the heating of an alkyl halide with a basic compound at an elevated temperature or an increased pressure or both, has been described by Dill.[8] According to Szarvasy,[9] methanol is conveniently prepared by heating methyl chloride with an alkaline reagent at elevated temperatures and pressures of 20 to 24 atmospheres. For example, by heating 520 grams of methyl chloride, 3500 grams of water and 330 grams of calcium oxide in a horizontally rotating iron container to 140° C. for two hours, the pressure rising to about 20 to 24 atmospheres, 96 per cent of the theoretical amount of methanol is obtained. The walls of the reaction vessel become coated with the alkaline solution which prevents corrosion.

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[6] *Compt. rend.*, 1857, 45, 916; *Ann. chim. phys.*, 1858, (3), 52, 101.

[7] British Patent 20,550, 1914; *J.S.C.I.*, 1915, 34, 575; U. S. Patent 1,253,055, Jan. 8, 1918; *Chem. Abs.*, 1918, 12, 702; both patents assigned to Roessler and Hasslacher Chemical Co.

The process of Riesenfeld[10] involves the intermediate formation of dimethyl ether by heating methyl chloride, under pressure in anhydrous alcoholic solution, with caustic alkalies. The dimethyl ether, so obtained, is subsequently hydrolyzed under pressure in the presence of a little free acid to yield methanol.

A method described by the Deutsche Petroleum A.-G.[11] involves passing gaseous methyl chloride countercurrent to a stream of a molten mixture of equimolecular quantities of sodium and potassium acetates at a temperature of 250° C. Methyl acetate and sodium and potassium chlorides are formed but the reaction must not be carried too far as the mixture becomes too viscous. The methyl acetate, which distils from the reaction vessels, is hydrolyzed with a solution of equimolecular quantities of sodium and potassium hydroxides to yield methanol and the mixed acetates of these metals, the latter being used again in the process. Increased pressures favor the formation of methyl acetate in this process. As an example it is reported that in 2½ hours, using 82 kilograms of sodium acetate and 98 kilograms of potassium acetate, 50 kilograms of methyl chloride can be converted into 30 kilograms of methanol, the yield being, therefore, over 90 per cent.

MacMullen and Gegenheimer[12] have developed a process of converting alkyl halides into alcohols, especially of methyl chloride into methanol, in which a mixture of the alkyl halide and steam (equimolecular proportions are said to be adequate) at a pressure of 175 to 200 lbs. per square inch is led over a contact mass of hydrated lime at 350° to 450° C., using a time of contact of 40 seconds or more. An apparatus for carrying out this process has been described by these workers,[13] in which two procedures can be adopted. In one, the mixture of methyl chloride and steam is passed through each of a plurality of conversion chambers, which are continuously charged with freshly hydrated lime at equal intervals of time. In another, the gaseous reaction mixture is passed successively through a series of conversion chambers containing progressively fresher hydrated lime and, as the lime in each chamber is consumed, the chamber is recharged with fresh lime and connected in at the other end of the series so that, in effect, the methyl chloride is contacted with the lime in countercurrent. A nearly complete conversion of the methyl chloride and consumption of lime is said to be thus effected.

Weber and Erasmus[14] described a method of treating a mixture of methyl chloride and methylene dichloride, produced by the controlled chlorination of methane, which consists essentially in forcing the mixture in gaseous form into a reaction vessel wherein it is heated under pressure with milk of lime. The methyl chloride is said to be hydrolyzed and the unattacked methylene dichloride is passed in gaseous form into a cooling apparatus where it is liquefied.

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[8] French Patent 477,812, 1914; *Chem. Abs.*, 1916, **10**, 1407.

[9] U. S. Patent 1,181,697, May 2, 1916; *Chem. Abs.*, 1916, **10**, 1693.

[10] U. S. Patent 1,379,362, May 24, 1921; *Chem. Abs.*, 1921, **15**, 3290.

[11] German Patent 367,204, 1920; *J.S.C.I.*, 1923, **42**, 576A.

[12] U. S. Patent 1,549,779, Aug. 18, 1925; assigned to Mathieson Alkali Works, Inc.; *Chem. Abs.*, 1925, **19**, 3490; *J.S.C.I.*, 1925, **44**, 828B.

[13] U. S. Patent 1,641,544, Sept. 6, 1927; assigned to Mathieson Alkali Works (Inc.); *Chem. Abs.*, 1927, **21**, 3369.

[14] U. S. Patent 1,565,345, Dec. 15, 1925; *Chem. Abs.*, 1926, **20**, 424; British Patent 227,475, 1925; *J.S.C.I.*, 1925, 784B; both patents assigned to T. Goldschmidt A.-G.

Carter and Coxe[15] reported a process for the hydrolysis of alkyl halides to alcohols, particularly methyl chloride to methanol, by heating under pressure with an aqueous alcoholic solution of an alkali (or alkaline earth) hydroxide at temperatures of about 100° C. The relative amounts of ether and alcohol produced in this hydrolytic process depend mainly upon the concentration of alcohol in the liquid. The experimental figures in Table 134, referring to the hydrolysis of methyl chloride in a methanol-water solution of calcium hydroxide, are advanced in support of this contention.

TABLE 134.—*Hydrolysis of Methyl Chloride by Calcium Hydroxide in Aqueous Methanol.*

Concentration of Methanol	Conversion	
	To Alcohol	To Dimethyl Ether
80	22.1	77.9
60	30.8	69.2
20	79.7	20.3
10	83.4	16.6
5	88.4	11.6

In order, therefore, to minimize the formation of ether during the hydrolysis it is proposed to keep the alcohol concentration in the reaction liquid at somewhat above 5 per cent but not exceeding 20 per cent. Starting with a 5 per cent methanol solution, for example, the hydrolysis of methyl chloride may be carried on until the concentration of the methanol rises to 10 to 15 per cent when the process is stopped. A considerable excess of alkali over that required for reaction is advantageous. For example, 100 pounds of methyl chloride are added to a solution of 150 pounds of sodium hydroxide in 100 gallons of 5 per cent aqueous methanol in an autoclave, and the mixture is heated at 100° C. until reaction is complete (about 1 hour). Sodium chloride, methanol, and some methyl ether are produced.

McKee's process[16] for the conversion of methyl chloride into methanol consists in mixing this gas with an equal volume of steam and passing it over an alkaline-earth hydroxide, especially calcium hydroxide, at 350° to 375° C. in an aluminum tube. The aqueous solution obtained by cooling the issuing gases affords methanol, free from acetone, and some dimethyl ether. The yield of methanol may exceed 70 per cent of the theoretical under the above conditions.

Silica or porous dioxides of the silica group have been suggested by Lloyd and Kennedy[16a] as catalysts for the production of alcohols or phenols from alkyl or aryl chlorides by reaction with steam at 550° to 850° C.

Methanol is a colorless liquid, boiling about 66° C., miscible in all proportions with water and most organic solvents. Until recent years the sole method for its large scale production was by the destructive distillation of wood. However, an increasingly important method of manufacture is by the catalytic high pressure reduction of carbon monoxide in the presence of a catalyst.[16b] This synthetic method yields a very pure methanol which is rapidly displacing the somewhat impure product obtained by wood distillation. Although methanol finds extensive application as a solvent for varnishes, lacquers and celluloid products,

[15] U. S. Patent 1,566,818, Dec. 22, 1925; assigned to Karpen and Bros.; *Chem. Abs.*, 1926, **20**, 424.

[16] U. S. Patent 1,688,726, Oct. 23, 1928; *Brit. Chem. Abs.* **B**, 1929, 511.

[16a] U. S. Patent 1,849,844, Mar. 15, 1932; *Chem. Abs.*, 1932, **26**, 2747.

[16b] See Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 1930, 652.

its main use is as a chemical intermediate notably for the production of formaldehyde (a substance used in vast quantities in the manufacture of synthetic resins and as a disinfectant) and as a methylating agent in industrial organic synthesis. A possible important application of methanol is as a constituent of motor fuels and as an anti-freeze in automobile radiators. Methanol vapor is stated to be definitely toxic.

PRODUCTION OF ESTERS AND ETHERS FROM METHYL CHLORIDE

The process of the Deutsche Petroleum A.-G.[17] involving the intermediate production of methyl acetate by passing methyl chloride countercurrent to a stream of a molten mixture of sodium and potassium acetates at 250° C. has already been discussed. According to Carter and Coxe,[18] methyl acetate may be produced by heating methyl chloride with sodium acetate in the presence of water and a solvent for the methyl chloride, such as alcohol, in an autoclave at 100° C. The reaction is said to be rapid with a nearly theoretical yield, and is also applicable to the production of other methyl esters and of esters derived from higher alcohols, i.e., by interaction with higher alkyl halides.

Methyl acetate has been utilized to some extent as a substitute for acetone in certain of its applications as solvents. It is a good solvent for cellulose nitrate and for various resins but is readily hydrolyzed.

The production of *ethers* from alkyl halides, such as methyl or ethyl chloride, was reported by Carter and Coxe [19] to be readily effected by heating such alkyl halides under pressure in the presence of an alcohol and an alkaline compound such as caustic soda or potash. The formation of methyl ethyl ether from methyl chloride, ethanol and caustic soda is said to take place readily at 100° C. in an autoclave, sodium chloride being deposited.

CONVERSION OF ETHYL CHLORIDE INTO ETHANOL AND ITS DERIVATIVES

Little work appears to have been done on the hydrolysis of ethyl chloride to ethanol by steam in the vapor phase, in contact with alkaline hydroxides, or in the liquid phase. Aqueous potash slowly converts ethyl chloride into ethanol on heating but quantities of *ether* are obtained by heating concentrated alcoholic potash and ethyl chloride at 100° C. in a sealed tube.[20] By passing ethyl chloride over soda-lime at 350° C., Nef [21] obtained a 30 per cent conversion into ethanol. At the same time some sodium acetate, methane and hydrogen were formed. The first reaction can be represented as

$$CH_3CH_2Cl + NaOH \longrightarrow NaCl + CH_3CH_2OH$$

In attempting to explain the formation of the other products it was suggested that ethyl chloride first undergoes an ethylidene dissociation, such as

$$CH_3CH_2Cl \longrightarrow CH_3CH< + HCl$$

Both of these latter substances then react with the alkali; the hydrogen chloride yielding salt and water, and the ethylidene group (or radical) yields an acetate and hydrogen. There is also the possibility that some alcohol would be formed as an intermediate oxidation product of the ethylidene group by the alkali. Decomposition of the sodium acetate yields methane and hydrogen together with sodium carbonate.

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[17] German Patent 367,204, 1920; *J.S.C.I.*, 1923, **42**, 576A.

[18] U. S. Patent 1,459,971, June 26, 1931; *Chem. Abs.*, 1923, **17**, 3033; British Patent 220,721, 1923; *J.S.C.I.*, 1924, **43**, 850B; both patents assigned to S. Karpen and Bros.

[19] U. S. Patent 1,459,177, June 19, 1923; *Chem. Abs.*, 1923, **17**, 2886.

[20] Balard, *Ann. chim. phys.*, 1884, (3) **12**, 302; see Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1853, **8**, 372.

[21] *Ann.*, 1899, **309**, 126; 1901, **318**, 1; *J.A.C.S.*, 1904, **26**, 1549.

According to Müller-Cunradi [22] ethyl chloride may be converted into ethanol by passing it in the presence of excess of steam over a heated contact material, which does not combine with hydrochloric acid. For example, a mixture of ethyl chloride and 10 times its weight of steam, passed at 250° C. over active charcoal impregnated with 5 per cent of zinc sulphate, undergoes practically quantitative conversion into ethanol. The point of equilibrium in the reversible gaseous reaction, $C_2H_5Cl + H_2O \rightleftarrows C_2H_5OH + HCl$, has not apparently been determined at the temperature mentioned above, but, by analogy with the case of the hydrolysis of methyl chloride with steam at elevated temperatures, it is doubtful whether the equilibrium is favorable to this process. The velocity of the reaction

$$C_2H_5OH + HCl \longrightarrow C_2H_5Cl + H_2O$$

in the liquid phase at 110° C. was investigated by Kilpi.[23] The rate of reaction between hydrochloric acid and the alcohol increased more rapidly with the temperature than that of the opposing reaction between ethyl chloride and water.

A process for the manufacture of dialkyl ethers from alkyl halides and in particular of *diethyl ether* from ethyl chloride has been described by Lacy,[24] who proposed to effect this conversion by passing ethyl chloride over heated granular calcium oxide at elevated temperatures. The reaction which is said to occur, namely:

$$2C_2H_5Cl + CaO \longrightarrow (C_2H_5)_2O + CaCl_2,$$

is highly exothermic, and, in order to control the process, Lacy suggested diluting the ethyl chloride vapors with ethane. Thus, a mixture of 1 volume of ethyl chloride and 4 volumes of ethane is passed over granular, or powdered, calcium oxide at 250° to 450° C. The resulting gaseous mixture is led through a cooler, compressed to 10 atmospheres and finally cooled to —20° C., whereby the diethyl ether is separated in the liquid state.

The production of diethyl ether by reaction of ethyl chloride under pressure with ethanol in the presence of an alkaline compound was reported by Carter and Coxe,[25] who also produced *ethyl esters,* such as ethyl butyrate, by heating ethyl chloride under pressure with a sodium salt of an organic acid in the presence of dilute alcohol.[26]

HYDROLYSIS OF HIGHER ALKYL HALIDES, ESPECIALLY CHLORIDES, TO ALCOHOLS

The applicability of vapor phase hydrolysis to alkyl halides of higher molecular weight is greatly reduced, mainly because of their greater tendency to undergo disruptive decomposition into an olefin and a halogen acid, according to the reaction: $C_nH_{2n+1}X \rightarrow C_nH_{2n} + HX$. This decomposition is perhaps the greatest difficulty associated with the hydrolysis of alkyl halides to alcohols, especially with chlorides, which are more difficult to hydrolyze than the bromides and iodides.

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[22] German Patent 413,447, 1921; assigned to Badische Anilin- und Soda-Fabrik; *J.S.C.I.,* 1925, 44, 784B.

[23] *Z. physik. Chem.,* 1914, 86, 427; *Chem. Abs.,* 1914, 8, 1378. Also, *Ann. Acad. Sci. Fennicae,* 1920, 16A, No. 3, 27; *Chem. Abs.,* 1923, 17, 2810.

[24] U. S. Patent 1,245,742, Nov. 6, 1917; assigned to Roessler and Hasslacher Chemical Co.; *Chem. Abs.,* 1918, 12, 279.

[25] U. S. Patent 1,459,177, June 19, 1923; assigned to Karpen and Bros.; *Chem. Abs.,* 1923, 17, 2886.

[26] U. S. Patent 1,459,971, June 26, 1923; assigned to Karpen and Bros.; *Chem. Abs.,* 1923, 17, 3033.

The alkyl iodides are much more readily hydrolyzed than the other halides but this fact is of little industrial value since the iodides cannot be produced by direct iodination of hydrocarbons. The matter is also further complicated by the great differences in ease of hydrolysis of the primary, secondary and tertiary halogen derivatives of the homologues of ethane. As a rule, the tertiary compounds are fairly readily hydrolyzed and the primary are the most difficult to convert into alcohols. The two extremes of behavior are exemplified by the *tertiary iodides,* which undergo extensive hydrolysis even in the presence of warm water, as contrasted with the *primary chlorides,* which require heating with strong caustic alkali solutions to temperatures of 150° C. or above to effect appreciable hydrolysis.

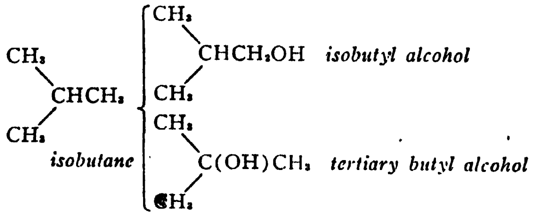
On account of the comparative high price of the bromine compounds and of the difficulty of producing iodine derivatives directly from paraffin hydrocarbons, it appears that only the alkyl chlorides are worthy of attention as commercial raw materials for the manufacture of alcohols. Our knowledge of the hydrolysis of the higher alkyl chlorides is almost entirely restricted to the chlorinated pentanes and isopentanes, which have been extensively investigated during the last few years. As far as is known, practically no investigations have been carried out on the hydrolysis of the monochlorides derived from propane, n-butane, and isobutane but such conversions would appear to offer some commercial possibilities.

Propane is known to yield both of the possible monochlorides on chlorination at elevated temperatures. Of these, 2-chloropropane may be expected, by analogy with the chloropentanes, to be more readily hydrolyzable (to isopropyl alcohol) than the primary chloride. No data are available to show what conditions are necessary for effecting these hydrolyses.

In a similar way n-butane is capable of yielding both a primary and a secondary chloride which might be hydrolyzed to n-butanol and secondary butanol respectively, and isobutane can form only a primary and a tertiary chloride, but no secondary. The monochlorides derived from isobutane should thus be capable of yielding a primary alcohol (isobutyl alcohol) and tertiary butanol. Here again the conditions necessary for successful operation have not been specifically described although they are apparently similar to those used with the amyl chlorides.[27] The various alcohols which might be produced in this manner from propane and the butanes are the following:

$$\underset{\textit{propane}}{CH_3CH_2CH_3} \left\{ \begin{array}{ll} CH_3CH_2CH_2OH & \textit{n-propyl alcohol} \\ CH_3CHOHCH_3 & \textit{isopropyl alcohol} \end{array} \right.$$

$$\underset{\textit{n-butane}}{CH_3CH_2CH_2CH_3} \left\{ \begin{array}{ll} CH_3CH_2CH_2CH_2OH & \textit{n-butyl alcohol} \\ CH_3CHOHCH_2CH_3 & \textit{secondary butyl alcohol} \end{array} \right.$$



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[27] E.g., Ayres, Canadian Patent 278.537, 1928; *Chem. Abs.*, 1928, 22, 2753.

CONVERSION OF MONOCHLOROPENTANES TO AMYL ALCOHOLS

In considering the hydrolysis of the various monochloro-derivatives of pentane and isopentane to the corresponding amyl alcohols, attention must be drawn to the sharply differentiated properties of the three principal types of monochlorides under these conditions. When the rates of hydrolysis of the three types of monochlorides by hot water alone are compared, it is found that whereas the tertiary compounds are appreciably hydrolyzed, the secondary are more slowly attacked, and the primary chlorides show no tendency to undergo hydrolysis. On the other hand, the order of reactivity of the chlorides is reversed in their reactions with salts of organic acids in homogeneous solutions at, say, 180° C. In this case, the primary chlorides readily react to form esters, the secondary chlorides rather less rapidly and tertiary chlorides do not form esters under such conditions but tend to yield amylenes. During the hydrolysis of amyl chlorides either by water alone or by alkalies or aqueous solutions of alkali salts of the higher fatty acids, considerable quantities of amylenes are formed by elimination of hydrogen chloride according to the reaction $C_5H_{11}Cl \rightarrow C_5H_{10} + HCl$. The velocity of this decomposition increases rapidly with rising temperature and becomes appreciable at temperatures at which the velocity of hydrolysis is sufficiently great to give good yields of amyl alcohols. The production of amylenes is most rapid from the tertiary chlorides, less from secondary chlorides, and least from primary chlorides. According to Ayres,[28] the rates of decomposition of the three classes of amyl chlorides into amylenes and hydrogen chloride at 180° C. are as follows:

	Decomposition per Min. Per Cent
Primary	0.08
Secondary	0.65
Tertiary	3.70

As the temperature is reduced below 180° C. the ratio of rate of decomposition of secondary chlorides to rate of esterification remains the same but the rate of hydrolysis is not reduced nearly so rapidly as the rate of decomposition. On the other hand, the tertiary chlorides are readily hydrolyzed by water even at 100° C., at which temperature the tendency to decompose is relatively slight. Accordingly fairly low temperatures favor good yields of alcohols from secondary and tertiary chlorides. The primary chlorides are more difficult to hydrolyze and require higher temperatures and a catalyst.

According to Ayres, the rates of hydrolysis of primary, secondary and tertiary amyl chlorides in the presence of water alone are as given in Table 135.

TABLE 135.—*Rate of Hydrolysis of Amyl Chlorides in Water.*

	Agitated with Water at 80° C.	Heated in Colloidal Contact with Water at 180° C.
	Hydrolyzed per Min. —Per Cent—	
Tertiary	1.20	2.85
Secondary	0.05	0.60
Primary	0.00	0.00

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[28] *Ind. Eng. Chem.*, 1929, 21, 899.

Although the presence of alkali or dilute acid does not accelerate the rate of hydrolysis, addition of the former material removes the hydrochloric acid formed from the sphere of the reaction and so displaces the equilibrium

$$C_5H_{11}Cl + H_2O \rightleftharpoons C_5H_{11}OH + HCl$$

to the right. It will be noted that the rate of hydrolysis of the primary chlorides is very low even at 180° C. so that it becomes necessary to hasten this reaction in order to obtain the primary alcohols on a commercial scale. The solution of this problem has been achieved by taking advantage of the high velocity of esterification of primary chlorides in the presence of alkali salts of certain fatty acids. In practice it appears only necessary to have present in the reaction mixture a quantity of a fatty acid together with an excess of aqueous alkali. Under these circumstances the primary chloride is first esterified and the ester so formed is immediately hydrolyzed to the alcohol. The hydrolysis of primary chlorides to alcohols by alkali is thus hastened by the addition of fatty acids. For this purpose oleic and stearic acids are especially valuable because, by virtue of the colloidal characteristics of their salts, they facilitate intimate contact between the amyl chloride and the hydrolyzing medium.

Previous to the work of Ayres and his collaborators, Essex, Hibbert and Brooks[29] investigated the hydrolysis of mixtures of monochloropentanes (primary and secondary) by means of aqueous solutions of alkalies, at temperatures of 190° to 300° C. and at pressures of 240 to 6000 lbs. per square inch. The yield of amyl alcohols obtained was practically the same with sodium carbonate as with sodium hydroxide but sodium acetate gave a higher yield than either under the same conditions. Besides amyl alcohols, amylenes and quantities of diamyl ether (not exceeding about 8 per cent) were obtained. By heating 213 grams of chloropentane with 740 cc. of 25 per cent sodium hydroxide for 8½ hours at 250° C. under a pressure of 1200 lbs. per square inch, the yield of amyl alcohol was 20.5 per cent, and a maximum yield of 28 per cent was obtained using 580 cc. of alkali at 210° C. under a pressure of 3300 lbs. per square inch. These results show the difficulty of this hydrolysis.

Summarizing, it may be said that the hydrolysis of amyl chlorides by aqueous alkali in the liquid phase is a matter of some difficulty, requiring fairly high temperatures (150° C. or over). The primary chlorides are most difficult to hydrolyze and the tertiary chlorides least so. On the other hand, the tertiary chlorides have the greatest tendency to decompose into amylene and hydrogen chloride, an undesirable transformation, and the primary chlorides are most stable in this respect. In order to reduce the temperature necessary for the hydrolysis of the difficultly hydrolyzable primary compounds, the addition of soaps of high molecular weight fatty acids (oleic and stearic acids) has been found highly advantageous. The soap not only acts as an esterifying agent, yielding a readily hydrolyzable ester, but also promotes intimate contact of reagents.

THE LARGE SCALE PRODUCTION OF AMYL ALCOHOLS

The large scale manufacture of these alcohols has been described by Ayres[30] and by Clark.[31] The mixture of n- and iso-pentanes, employed in this process, is obtained by the low temperature distillation of natural gas gasoline. The chlorination of such a mixture has been previously discussed in Chapter 30. The mixture of monochlorides, derived from n- and iso-pentanes and containing six isomeric compounds, is subjected to hydrolysis by the action of 30 per cent aqueous caustic soda in the presence of a catalyst (sodium stearate or oleate). These soaps accelerate the hydrolysis of the more difficultly hydrolyzable primary chloride and favor the process generally by assisting emulsification and intimate contact of reactants. The operation of mixing and digesting chlorides, aqueous caustic solution and oleate, and distilling off the alcohols and amylenes was first conducted as a batch process[32] but the steps were later made continuous by joining two digesters, maintaining one full all the time, continuously circulating between the two, and distilling from the second, partly filled. Amyl chloride and aqueous caustic soda are continuously pumped into a hot emulsion of amyl alcohol and water circulating rapidly through a digester, from which are continuously withdrawn two products, namely (1) a saturated salt solution which is returned to electrolytic cells for the manufacture of chlorine and caustic soda; and (2) a vapor consisting principally of mixed amyl alcohols. This vapor is separated by a train of fractionating columns into five components: (a) amyl chloride, which is returned for hydrolysis; (b) amylenes which are hydrated to (secondary and tertiary) alcohols; (c) diamyl ether; (d) amyl alcohol fractions which are cut for special purposes; and (e) a mixture of amyl alcohols marketed as a pyroxylin lacquer solvent under the name of "Pentasol."

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[29] *J.A.C.S.*, 1916, 38, 1368; *J.S.C.I.*, 1916, 35, 906.

[30] *Ind. Eng. Chem.*, 1929, 21, 899.

[31] *Ind. Eng. Chem.*, 1930, 22, 439; *Chem. Met. Eng.*, 1931, 38, 206; see also Kirkpatrick, *Chem. Met. Eng.*, 1927, 34, 276; Garlick, *Ind. Chemist*, 1928, 4, 363; *Chem. Abs.*, 1929, 23, 454.

The actual temperature used in the hydrolysis of amyl chlorides is not definitely stated but it is probably in the neighborhood of 150° C. It is obviously essential for good yields of amyl alcohols from the three types of chlorides, exhibiting such markedly different behavior on hydrolysis, to choose such operating conditions that, on the one hand, even the difficultly attacked primary chlorides are hydrolyzed with sufficient speed, and on the other hand, the velocity of decomposition of the tertiary chlorides (into amylene and hydrochloric acid) is still relatively low. As with many other chemical processes it became necessary to effect a compromise between two opposing factors. No method of operation can effect complete hydrolysis of the mixture of amyl chlorides and it is a matter of the greatest difficulty to remove the last traces of them from the hydrolyzed alcohols. Thus several hours digestion of amyl alcohol containing 1 per cent of amyl chloride with 5 per cent of metallic sodium only reduces the amyl chloride content to about 0.3 per cent. Fortunately a very satisfactory separation of amyl chlorides and alcohols may be effected by fractional distillation in the presence of water. The chlorides and alcohols form a three-component constant boiling mixture with water, the distillate from which separates on cooling into two layers, an aqueous layer containing alcohol in solution and a non-aqueous layer containing 20 per cent of alcohols and 80 per cent of chlorides.

OTHER METHODS FOR THE PRODUCTION OF AMYL ALCOHOLS

Hibbert, Essex and Brooks[33] described a method of making a material similar to fusel oil containing amyl and hexyl alcohols by hydrolysis of the monochlorides of pentanes and hexanes obtained by the chlorination of a gasoline distillate boiling between 25° and 75° C. The hydrolysis is effected by subjecting the mixed amyl and hexyl chlorides to the action of alkali or alkali carbonate solution under a pressure of 1000 to 4000 lbs. per square inch at temperatures of

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[32] Ayres and Haabestad, U. S. Patent 1,691,426, Nov. 13, 1928; *Brit. Chem. Abs.* **B**, 1929, 11; Canadian Patent 286,076, 1929; *Chem. Abs.*, 1929, 23, 1417; British Patent 241,889, 1925; *Brit. Chem. Abs.* **B**, 1927, 859; all patents assigned to B. A. S. Co.

[33] U. S. Patent 1,214,919, Feb. 6, 1917; assigned to Gulf Refining Co.; *Chem. Abs.*, 1917, 11, 1019.

180° to 280° C. A pressure of 3000 lbs. per square inch and a temperature of 220° C. are recommended to give a 40 per cent yield of synthetic fusel oil. The pressure may be attained either by the application of heat alone or by the addition to the charge of a light volatile liquid such as ordinary ether. These high pressures are said to increase materially the yields of alcohols but considerable quantities of alkyl chlorides are always converted into olefins, i.e., amylenes and hexenes. It has been proposed to convert these olefins into (secondary and tertiary) alcohols by absorption in commercial sulphuric acid d 1.86 (at 0° C.), followed by dilution and distillation.

A second, and indirect, method of hydrolysis of amyl and hexyl chlorides consists, according to the same workers, in heating under a pressure of 300 lbs. per square inch or more at 170° to 250° C. with sodium acetate, either with or without a solvent. A mixture of the corresponding amyl and hexyl acetates together with a mixture of olefins is formed. The acetates may be readily hydrolyzed to the corresponding alcohols by the usual methods.

A process of Brooks and Essex [34] for the manufacture of amyl alcohols and other high boiling monohydric alcohols from the corresponding monochlorinated paraffins, consists in heating the chloride under pressure with a mixture of methyl alcohol and a formate. A mixture consisting of a metallic chloride, methyl formate, and the desired amyl or other alcohol is produced. For example, 1 gallon of monochlorinated pentane (or homologous paraffin hydrocarbon) mixture, 3 to 4 gallons of methyl alcohol and 6 pounds of commercial dry sodium formate are introduced into a suitable pressure vessel, which can be rotated. The mixture is heated in this sealed container to about 160° C. for about 6 hours. The methyl formate produced in the reaction may be continuously removed through a weighted valve but this is unnecessary. By retaining the methyl formate in the reaction mixture the progress of the operation may be followed by readings on a pressure gauge, the end of the reaction being indicated by no further increase of pressure. The reaction mixture is then cooled and separated from the insoluble salts, consisting mainly of sodium chloride. Distillation of the salt-free liquid yields first methyl formate (boiling point 32° to 33° C.), then methyl alcohol (boiling 66° to 67° C.) and finally a mixture of amyl and other high boiling alcohols. The methyl formate is hydrolyzed by caustic alkali to methyl alcohol and an alkali formate, both of which are used again.

The hydrolysis of amyl and hexyl chlorides to the corresponding alcohol by first converting them into readily hydrolyzable esters of stearic acid (or other non-corrosive fatty acid of high-boiling point) has been suggested.[35] Stearic acid and solid caustic soda are heated together in a jacketed vessel at 200° to 240° C., and when all excess water has been expelled, a mixture of monochlorinated pentanes and hexanes is introduced at the bottom of the vessel. Part of the halogenated hydrocarbon mixture reacts with the sodium stearate forming esters of stearic acid, another portion is converted into olefins, and the rest distils unchanged. The volatile products are condensed and separated by a reflux cooler maintained at the requisite temperature. The stearic ester in the reaction vessel is cooled to 150° C., treated with sufficient caustic soda to replace the alkali which has reacted with the chlorides, heated again to 200° to 240° C., and the resulting alcohols are distilled off with a little water or steam.

Ayres [36] described a process of producing monohydric alcohols containing 4 or 5 carbon atoms by chlorination of n-butane and n-pentane followed by hydrolysis of the alkyl chlorides with aqueous alkali. The resulting alcohols are purified from chlorides by extraction with water. The hydrolysis of mixed amyl chlorides is also accomplished by heating with aqueous alkali and a substantially water-insoluble organic acid in a closed vessel at 150° C. The organic ester produced is heated in a closed vessel at the same temperature with further quantities of amyl chlorides, and aqueous caustic soda and the amyl alcohols produced are separated by fractionation.[87]

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[34] U. S. Patent 1,221,667, Apr. 3, 1917; assigned to Gulf Refining Co.; *Chem. Abs.*, 1917, **11**, 1885.
[35] E. I. DuPont de Nemours and Co., Inc., British Patent 119,249, 1917; *J.S.C.I.*, 1918, **37**, 717A.
[36] Canadian Patent 278,537, 1928; assigned to B. A. S. Co.; *Chem. Abs.*, 1928, **22**, 2753.

Zinc oxide has also been suggested as a base for the hydrolysis of amyl chloride to amyl alcohol.[87a]

PRODUCTION OF AMYL ESTERS FROM CHLOROPENTANES

The classical method of preparation of alkyl esters of organic acids by the direct combination of an alkyl halide with the anhydrous salt of an organic acid has been applied by a number of workers to the production of amyl esters from monochlorinated pentanes. Some data on this type of reaction have been supplied by Ayres.[88] The comparative figures are given in Table 136 for the rates of esterification of the primary, secondary and tertiary amyl chlorides by potassium acetate in glacial acetic acid solution at 180° C.

TABLE 136.—*Rates of Esterification of Amyl Chlorides with Potassium Acetate at 180° C.*

	Esterified per Min. Per Cent
1-Chloropentane	3.17
1-Chloro-2-methylbutane	3.17
4-Chloro-2-methylbutane	1.20
Secondary amyl chlorides	0.60
Tertiary amyl chlorides	0.00

The figures in Table 136 reveal the fact that the primary chlorides are much more readily esterified than secondary chlorides. Dry esterification (in the absence of water) of tertiary amyl chloride does not yield an ester but only trimethylethylene. The above rates of reaction are approximately doubled for a temperature rise of 10° C. and are of the same order with the potassium, sodium, or calcium salts of acetic, butyric, oleic, and stearic acids provided the salts are in molecular contact with the amyl chloride. This problem of intimate contact is simplified in the case of the higher fatty acids, the salts of which serve to emulsify the reaction mixture. According to Ayres, the esterification of secondary amyl chlorides in the absence of water yields about 48 per cent of the ester but in the presence of water the yield varies from 65 per cent at 180° C. to almost theoretical at 100° C. As in hydrolysis, the yields are reduced by decomposition of these chlorides into amylene and free hydrogen chloride. This decomposition is greatest in the case of the tertiary, and at a minimum with primary chlorides. The formation of amylenes from amyl chlorides is, fortunately, not accelerated by moisture, caustic soda, amyl alcohol and esters or fatty acids.

Among the earlier studies of the conversion of amyl chlorides into acetates, that of Brooks, Smith and Essex[89] is of interest. A mixture of chlorinated pentanes, boiling between 95° and 140° C. and containing about 90 per cent of (mixed) monochlorides, was acetylated by heating under pressure with sodium acetate and acetic acid in the presence of a solvent (alcohol, acetone, or amyl acetate). Yields of amyl acetate varying from 55 per cent to 63 per cent of the theoretical were obtained by heating the reaction mixture for 5 to 9 hours at 195° to 200° C. under a pressure of 180 to 230 lbs. per square inch, though at the same time quantities of amylenes were always produced.

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[87] Ayres and Haabestad, U. S. Patent 1,691,426, Nov. 13, 1928; *Brit. Chem. Abs.* **B**, 1929, 11; Canadian Patent 286,076, 1929; *Chem. Abs.*, 1929, **23**, 1417; British Patent 241,889, 1925; *Brit. Chem. Abs.* **B**, 1927, 859; all patents assigned to B. A. S. Co.

[87a] Masland, U. S. Patent 1,086,381, Feb. 10, 1914; *Chem. Abs.*, 1914, **8**, 1330.

[88] *Ind. Eng. Chem.*, 1929, **21**, 899.

[89] *J. Ind. Eng. Chem.*, 1918, **10**, 511.

Koch and Stallkamp[40] have described a method of esterification of amyl chlorides in which the tendency of these amyl chlorides to decompose into amylenes and hydrogen chloride is said to be suppressed by the introduction of activated charcoal as a catalyst,[41] The esterification is carried out by mixing the amyl chloride along with 65 to 75 parts by weight of fused and ground sodium acetate and 1 to 2 parts of solvent in a steel-jacketed, agitator-equipped autoclave, which is then heated to 400° to 450° F. (pressure, 200 to 250 lbs. per sq. in.) for about 8 hours. The esterified product is distilled directly from the autoclave through a condenser into a washer where it is washed and neutralized with sodium carbonate solution, and again distilled to yield the following fractions:

Fraction 1, boiling up to 82° C., Amylenes, pentanes, etc.
Fraction 2, boiling 82° to 120° C., Unconverted amyl chloride and some esters.
Fraction 3, boiling 120° to 175° C., Amyl acetate.

The amyl acetate recovered in fraction 3 had the following properties: d 0.88; color, none; moisture, none; acidity, 0.196 per cent as acetic acid. It compared favorably with the technical grade of amyl acetate.

The influence of the addition of activated charcoal to the reaction liquid is clearly brought out by the figures in Table 137 of yields of ester obtained in comparative experiments with and without the addition of charcoal.

TABLE 137.—*Comparative Yields of Amyl Acetate from Amyl Chloride with and without Activated Charcoal.*

No Charcoal		Charcoal Used	
Duration of Run	Amyl Acetate Per Cent	Duration of Run	Amyl Acetate Per Cent
7 hours	37.2	7 hours 30 min.	58.2
6 hours 40 min.	29.2	8 hours 15 min.	83.2
7 hours 20 min.	35.4	8 hours	78.3

Yields of amyl acetate as high as 90 per cent of the theoretical were obtained by Dobryanski and Gurevich[42] by heating amyl chlorides (obtained by the photochemical chlorination of a fraction of Krasnodar aviation gasoline, boiling 31° to 38° C.) with dry sodium acetate at 230° C. in sealed tubes for 4 to 8 hours.

According to Clark,[43] it is better to produce amyl esters by direct esterification of the alcohols resulting from the hydrolysis of amyl chlorides than by direct esterification of the chlorides. Since the tertiary alcohol cannot be directly esterified by the use of ordinary reagents, this alcohol is first removed from the mixture of amyl alcohols, which are then acetylated in a kettle at 125° C. in the presence of sulphuric acid as a catalyst. The crude esters are neutralized with soda ash and purified by fractionation. The production of mixed amyl phthalates by direct esterification of "pentasol" with phthalic anhydride was described by

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[40] Koch and Burrell, *Ind. Eng. Chem.*, 1927, 19, 442.

[41] U. S. Patent 1,374,666, May 12, 1921; assigned to Ohio Fuel Supply Co.; *J.S.C.I.*, 1921, 40, 412A.

[42] *Neft. Khoz.*, 1928, 15, 532; *Brit. Chem. Abs.* **B**, 1930, 131.

[43] *Ind. Eng. Chem.*, 1930, **22**, 439.

Jaeger.[44] The product, boiling at 190° to 205° C. at 10 mm., is colorless or slightly yellow after rectification and is a solvent and plasticizer.

OTHER METHODS FOR THE PRODUCTION OF AMYL ESTERS

Masland[45] reported that good yields of amyl acetate may be obtained by heating a mixture of equal weights of monochloropentanes and acetic acid together with sufficient sodium acetate to combine with all the chlorine present. Acetic acid of 70 per cent concentration or higher may be employed. The reactants are heated in a sealed pressure container to a temperature of 180° C. or higher and under a pressure of about 250 lbs. per square inch. The period of heating may vary from 2 to 12 hours, longer periods being required with lower temperatures. The products consist of amyl acetate together with quantities of unsaturated hydrocarbons. The same worker[46] also suggested that the process can be modified so that the reaction mixture, consisting of amyl (or hexyl) chlorides, sodium acetate, and acetic acid (of concentrations down to 70 per cent) is subjected to a preliminary heating at 150° C. and 100 lbs. per square inch pressure for several hours. This treatment results in the production of olefins from the more readily decomposable chlorides. The olefins so formed are removed as far as possible by distillation, and the residual reaction mixture is then heated to 180° C. or higher at 250 lbs. per square inch pressure, at which time the main esterification takes place.

Kaufler[47] stated that the esterification of amyl chlorides by means of sodium acetate is greatly facilitated by the employment of sodium acetate prepared in a highly porous and bulky condition. By heating 100 parts by weight of amyl chloride, 72 parts of this grade of sodium acetate and 6 parts of glacial acetic acid under pressure for 12 hours at 195° to 210° C., a yield of 65 parts by weight of amyl acetates, boiling at 120° to 146° C., is obtained. The efficiency of esterification is enhanced by the addition of catalysts, such as copper salts, to the reaction mixture. Using quantities of reactants identical with those given above but with the addition of 3 parts by weight of copper acetate, the same yield of amyl acetates was obtained by operating at a lower temperature and for a shorter time, e.g., by heating at 170° to 180° C. for 8 hours.

Sparre[48] described a process for the manufacture of a nitrocellulose solvent by the acetylation of a mixture of mono- and di-chlorinated paraffin hydrocarbons (pentanes and hexanes) with sodium acetate and acetic acid. The composition of the solvent mixture obtained in this manner was approximately 35 per cent of olefins, 5 per cent of chloro-olefins, 50 per cent of monoacetates and 10 per cent of diacetates.

A process of Essex and Brooks[49] for the manufacture of amyl and similar esters from monochlorinated petroleum fractions involves heating the dry monochloride mixture with an equal weight of dry fused alkali salt of a fatty acid. The reaction is carried out in an autoclave at a temperature of about 200° C., and in the presence of a solvent such as acetic acid or preformed ester. For making esters of acetic acid, the sodium, potassium, or calcium salts of this acid may be employed while, if other esters are desired, such as formates, butyrates, propionates, benzoates, etc., the corresponding alkali salts may be substituted. The period of reaction depends mainly upon the temperature employed, the use of higher temperatures rendering possible the employment of shorter reaction periods. Suitable times of reaction are 20 hours at 150° C., 5 hours at 200° C., and 2 hours at 220° C. For the manufacture of amyl acetate, good yields are secured by using 100 parts of a mixture of equal parts of chloropentane and sodium acetate, 64 parts of glacial acetic acid and 64 parts of amyl acetate and effecting the reaction at 200° C. for 5 hours under pressure in a rotating autoclave.

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[44] U. S. Patent 1,764,022, June 17, 1930; assigned to Selden Co.; *Chem. Abs.*, 1930, **24**, 3801.

[45] U. S. Patent 1,077,988, Nov. 11, 1913; assigned to E. I. DuPont de Nemours and Co., Inc.; *Chem. Abs.*, 1914, **8**, 400.

[46] U. S. Patent 1,095,013, May 28, 1914; assigned to E. I. DuPont de Nemours and Co., Inc.; *Chem. Abs.*, 1914, **8**, 2219.

[47] U. S. Patent 1,106,047, Aug. 4, 1914; *J.S.C.I.*, 1914, **33**, 890. British Patent 2,779, 1913; *J.S.C.I.*, 1913, **32**, 767.

[48] U. S. Patent 1,148,258, July 27, 1915; assigned to E. I. DuPont de Nemours & Co., Inc.; *J.S.C.I.*, 1915, **34**, 924. Also British Patent 29,963, 1912; *J.S.C.I.*, 1914, **33**, 502.

[49] U. S. Patent 1,197,019, Sept. 5, 1916; assigned to Gulf Refining Co.; *J.S.C.I.*, 1916, **35**, 1082.

For the *purification* of synthetic amyl acetate prepared from chlorinated pentanes, Essex and Humphrey [50] recommended heating it with metallic sodium and then washing with water. The relatively small amounts of chloro-compounds (which are objectionable since they reduce the solvent properties) cannot be removed by heating with metallic magnesium or with the zinc-copper couple. The amount of sodium required for this purification step is that equivalent to the combined chlorine present and ordinarily does not exceed 1 per cent or so of the weight of material. Thus by refluxing 125 parts by volume of a synthetic amyl acetate with 1 per cent of metallic sodium for 2 hours, followed by cooling, dilution with water, separation and drying over calcium chloride, a product was obtained of better odor and considerably enhanced solvent properties as compared with the original ester. This procedure is said to be equally applicable to the purification of amyl alcohol, amyl formate, and other amyl esters synthesized from chloropentanes. Another method for the purification of amyl acetate containing chlorohydrocarbons has been proposed by Oberfell and Boyd,[51] who made use of the solubility of amyl acetate in sulphuric acid, in which the impurities are not soluble. The purification therefore consists in fractionally distilling the esterified chlorohydrocarbons to remove olefin hydrocarbons formed during the reaction and then treating the residue with sulphuric acid. The latter dissolves amyl acetate and similar esters, leaving the other constituents unaffected. The two layers are separated and the amyl acetate is recovered from its solution in sulphuric acid either by dilution with water or by wet steam distillation.

For the manufacture of amyl acetate from chloropentane Oberfell and Boyd [52] recommended esterification in the presence of sodium or potassium sulphate which they believe minimizes the decomposition of the chloropentane into amylenes. By heating a charge of 100 parts (by weight) of chloropentane, 72 parts of fused alkali acetate, 0.5 parts of acetic acid, and 1 part of sodium or potassium sulphate in a mechanically stirred acid-resisting autoclave under pressure at a temperature of 195° C. for 8 to 14 hours, a 65 per cent yield of amyl acetates, boiling at 120° to 148° C., is obtained. The presence of more than a trace of water in the alkali acetate is stated to be detrimental, since it leads to increased formation of amylenes.[53] The esterified product may be removed from the autoclave by distillation under pressure. Another catalyst which is employed to suppress partly the undesirable decomposition reaction resulting in the formation of olefins and to increase the yield of ester is activated carbon, such as "batchite" or "dorsite."[54] Yields of about 75 per cent of the theoretical amount of amyl acetate are obtained by heating a mixture of chloropentane, sodium acetate and activated carbon, particularly batchite, with or without the addition of acetic acid, at 250° to 450° F. and a pressure of 200 to 225 lbs. per square inch in an autoclave provided with a mechanical stirring device.

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[50] U. S. Patent 1,233,333, July 17, 1917; assigned to Gulf Refining Co.; *Chem. Abs.*, 1917, 11, 2580.

[51] U. S. Patent 1,278,198, Sept. 10, 1918; assigned to Ohio Fuel Supply Co.; *Chem. Abs.*, 1918, 12, 2325.

[52] U. S. Patent 1,302,583, May 6, 1919; assigned to Ohio Fuel Supply Co.; *Chem. Abs.*, 1919, 13, 1863.

[53] This is apparently contradictory to the results obtained by Ayres (previously noted). These two conclusions, however, can be reconciled if it is assumed that the reaction between amyl chloride and alkali acetate is facilitated by the small amount of acetic acid acting as a mutual solvent. Water would tend to throw out the amyl chloride from the acetic acid-potassium acetate solution and slow up the esterification rate while olefin formation proceeds unchecked, hence giving a lower yield of acetate. Under the conditions mentioned by Ayres, the sodium oleate and amyl chloride mix in all proportions and water does not throw out the amyl chloride. (Hass, private communication.)

Carter and Coxe[55] suggested a procedure for the manufacture of esters in which a halogenated paraffin hydrocarbon is heated under pressure at 100° C. with a metallic salt of an organic acid in the presence of water and a solvent for the halogenated hydrocarbon, such as alcohol. The production of amyl esters as intermediate products in the hydrolysis of amyl chlorides (especially primary compounds) by heating a substantially water-insoluble fatty acid, amyl chloride, and aqueous caustic soda in a closed vessel at 150° C. is described by Ayres and Haabestad.[56]

PROPERTIES AND USES OF THE SYNTHETIC AMYL ALCOHOLS AND THEIR ESTERS

The amyl alcohols find very extensive application, especially in the form of their esters, as solvents for cellulose nitrate in the production of pyroxylin lacquers. Despite the many new solvents available for cellulose nitrate, amyl acetate still holds a high position in this respect. Until the discovery of the synthetic processes, outlined above, the main source of amyl alcohols was the so-called fusel oil which constitutes a by-product of the alcohol fermentation industries Ordinary fusel oil contains two amyl alcohols, both of which are primary (3-methylbutanol and 2-methylbutanol) as well as other primary alcohols including n-propanol, isobutanol, and n-hexanols. On the other hand the synthetic amyl alcohols from petroleum pentanes contain not only primary, but also secondary alcohols and a tertiary alcohol, the relative proportions of these alcohols depending mainly upon the method of chlorination and the conditions of hydrolysis. The process described by Ayres[56a] and Clark[56b] produces six, out of the possible eight, isomeric amyl alcohols. Of these, three are primary; two, secondary; and one, tertiary. This mixture of isomers possesses the following approximate composition: 50 per cent primary isoamyl alcohols, 25 per cent of primary n-amyl alcohol, and a residue of 25 per cent consisting of secondary and tertiary alcohols. The physical properties of these six amyl alcohols are listed in Table 138.

TABLE 138.—*Physical Properties of Amyl Alcohols.*

Amyl Alcohol	Dry B.P., ° C.	d_{20}^{20}	Aqueous Azeotrope B.P., ° C.
Pentanol-1	138	0.817	95.5
Pentanol-2	119	0.810	92.3
Pentanol-3	115.7	0.815	91.4
2-Methylbutanol-1	128	0.816	93.8
2-Methylbutanol-2	101.8	0.812	87.2
3-Methylbutanol-1	130.5	0.812	95.0

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[54] Koch and Stallkamp, U. S. Patent 1,374,666, Apr. 12, 1921; assigned to Ohio Fuel Supply Co.; *Chem. Abs.*, 1921, 15, 2641.

[55] U. S. Patent 1,459,971, June 26, 1923; assigned to Karpen & Bros.; *J.S.C.I.*, 1923, 42, 952A.

[56] Ayres and Haabestad, U. S. Patent 1,691,426, Nov. 13, 1928; *Brit. Chem. Abs.* B, 1929, 11; Canadian Patent 286,076, 1929; *Chem. Abs.*, 1929, 23, 1417; British Patent 241,889, 1925; *Brit. Chem. Abs.* B, 1927, 859; all patents assigned to B A. S. Co.

[56a] *Loc. cit.*

[56b] *Loc. cit.*

Synthetic amyl alcohol is not a solvent for cellulose esters or cumaron but dissolves ester gum, elemi, mastic, shellac, and other resins, but only partly in the case of dammar, and is miscible with castor and linseed oils. Its main application is in the form of its esters.

By far the most important of the amyl esters is the acetate, though the formate and propionate have also been used to a lesser degree. A grade of synthetic amyl acetate, which has been marketed under the name of "Pentacetate," consists of a mixture of esters derived from three primary and two secondary amyl alcohols. Tertiary amyl alcohol, though produced in the synthesis from pentanes, cannot be esterified by ordinary means. "Pentacetate" meets the following specifications:

Color	Water white
d_{20}^{20}	0.860–0.870
Acidity	Less than 0.03% as acetic acid
Non-volatile at 100° C.	Less than 0.02%
Water content	None
Halogen content	None
Petroleum hydrocarbons	None
Weight per gallon	7.2 lbs.
Distillation	100% above 126° C.
	95% above 130° C.
	75% above 135° C.
	25% above 140° C.
	End point not above 155° C.

The mixture of synthetic isomeric amyl acetates has solvent properties almost identical with that manufactured from fusel oil and the tolerance of a nitrocellulose solution for toluene is about the same as that of pure amyl acetate and secondary butyl acetate but not as high as that of n-butyl and ethyl acetates. Data on tolerance of nitrocellulose solutions to hydrocarbons, viscosities of nitrocellulose solutions, evaporation rates and solubility of resins in the synthetic amyl acetate have been supplied by Wilson and Worster,[57] and demonstrate the essential similarity of the properties of this solvent with those of amyl acetate derived from fusel oil.

Amyl acetate is an excellent solvent for cellulose nitrate, and like synthetic amyl alcohol can be used as a solvent for a number of resins. It is not a solvent for cellulose acetate. Pentacetate has been stated to possess a slight, though not dangerous, toxicity.[58]

Of the other amyl esters, *amyl formate,* which is also a solvent for cellulose nitrate and a number of resins, has been used instead of amyl acetate for special applications, including those involved in the manufacture of leather-cloth and of non-splintering glass. It lacks the disagreeable odor of amyl and n-butyl acetates and hence is preferable to these solvents for upholstery work. *Amyl propionate* possesses a milder odor and slower rate of evaporation than the acetate and has been used for brushing lacquers where lower evaporation rate is desired. Some of the amyl esters are finding application in the manufacture of synthetic fruit essences and perfumes and for such purposes the synthetic amyl esters should prove valuable raw materials. The main utilization of amyl esters, however, is in the manufacture of lacquers.

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[57] *Ind. Eng. Chem.,* 1929, 21, 592.

[58] Durrans, "Solvents," Chapman and Hall, London, 1930.

PRODUCTION OF HIGHER ALCOHOLS FROM HIGHER ALKYL HALIDES

So little work has been carried out on the hydrolysis of monochlorinated paraffins of more than five carbon atoms that it is profitless to enter into any discussion of their possible applications. So far the aliphatic alcohols of more than five carbon atoms have not been of as great industrial value as the butyl and amyl alcohols. When these higher alcohols are required in sufficient quantities for special purposes a number of synthetic methods are available for their production from the lower alcohols and also from carbon monoxide and hydrogen. The production of some of the hexanols from monochlorinated hexane can apparently be brought about in a manner analogous to that used for the hydrolysis of the amyl chlorides. A *hexyl ester* was prepared by Pelouze and Cahours [59] by direct esterification of a monochlorinated petroleum hexane fraction while a *heptyl ester* was similarly obtained by Schorlemmer [60] from a chlorinated petroleum heptane. These products were in all probability mixtures of isomers but their preparation shows the possibility of extending the processes, previously described, to higher members of the series.

Of considerable interest is the possibility of producing *glycerol,* the alcohol of all edible fats, from petroleum hydrocarbons. Both propylene dichloride and allyl chloride have been suggested as starting materials for this synthesis. Thus, McElroy [61] converted propylene, or gaseous mixtures containing propylene, to glycerol by first treating it with chlorine to obtain propylene dichloride, followed by further chlorination to 1,2,3-trichloropropane, a liquid boiling at 158° C. The latter chlorination may be carried out either in the liquid phase in the presence of iodine and light, or in the vapor phase in the presence of a catalyst, such as bone-black. The 1,2,3-trichloropropane is then hydrolyzed by heating under pressure with aqueous sodium bicarbonate solution or it may be heated with sodium acetate solution to furnish acetins which are subsequently hydrolyzed. The process may be varied by first producing the propylene chlorohydrins which are then subjected to chlorination either in the presence of glacial acetic acid or a saturated solution of sodium phosphate and phosphoric acid. The resulting dichlorohydrin is then hydrolyzed to glycerol.

A process of Essex and Ward [62] involves the conversion of allyl chloride into glycerol dichlorohydrin by treatment with hypochlorous acid, followed by hydrolysis of this product to glycerol. For example, a mixture of 225 parts of allyl chloride and 4000 parts of an aqueous solution containing 215 to 220 parts of sodium hypochlorite is cooled and vigorously stirred while carbon dioxide is introduced into the solution until a test shows only a trace of hypochlorous acid. The flow of carbon dioxide is discontinued and the stirring stopped and a little less than 400 parts of sodium carbonate are added. The reaction mixture is then boiled under reflux for 7 hours, after which time the yield of glycerol in the resulting liquid is said to be 82 per cent of the theoretical.

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[59] *Jahresbericht,* 1863, 527.

[60] *Ann.,* 1863, 127, 315.

[61] U. S. Patent 1,466,665, Sept. 4, 1923; assigned to Carbide and Carbon Chemicals Corp.; *Chem. Abs.,* 1923, 17, 3881.

[62] U. S. Patent 1,477,113, Dec. 11, 1923; *Chem. Abs.,* 1924, 18, 840.

Chapter 34

Miscellaneous Reactions of Halogen Derivatives of Paraffins and Cycloparaffins

Because of the great number of known halogenated derivatives of the paraffin and cycloparaffin hydrocarbons and the great variations in their chemical reactivity it is possible, in a discussion of this type, to list only a few of the more important chemical reactions of those derivatives which are likely to become commercially available. The chlorine derivatives alone are worthy of serious notice since bromine and iodine compounds are too expensive for large scale application. From a technical point of view the monochlorinated paraffins, or alkyl chlorides, are by far the most important, mainly because they can be used in chemical synthesis, for example as alkylating agents, and also because of their relative ease of preparation in a pure condition.

MISCELLANEOUS REACTIONS OF THE ALKYL HALIDES

The normal order of chemical reactivities of the alkyl halides is as follows: the iodides are generally more reactive than the bromides; the chlorides are least reactive. This generalization is, however, only true for one particular type of alkyl halide since constitutive influences play an important rôle in determining chemical reactivity. In most chemical processes, the primary halides are less reactive than the secondary compounds while the tertiary products undergo some reactions with amazing facility. The tertiary halides, though, are incapable of taking part in some of the reactions exhibited by the other two classes; for example, they do not react with salts of organic acids or with alcoholic ammonia to yield esters and amines respectively but, under the influence of these reagents, are transformed in large measure to the corresponding olefin.

The halogen atom in alkyl halides is often replaceable by another halogen atom merely by heating with certain metallic halides. For example, n-propyl iodide is partly converted into the corresponding chloride by the action of mercuric chloride. Many other examples of this interchange of halogens have been noted.

In the following pages a few of the more important reactions of the alkyl halides are briefly discussed, attention being concentrated more especially on the readily available alkyl chlorides. This account is not to be considered by any means exhaustive but it will serve to indicate some of the obvious applications, both actual and potential, of these compounds in chemical technology. Among the more interesting, and valuable, reactions of the alkyl halides, the following may be mentioned:

(1) Production of olefins and hydrogen halides by the reaction

$$C_nH_{2n+1}X \longrightarrow C_nH_{2n} + HX.$$

(2) Reaction with alkali alcoholates or phenates to yield ethers, thus:

$$C_nH_{2n+1}X + NaOR \longrightarrow C_nH_{2n+1}OR + NaX,$$

where R = alkyl or aryl group.

(3) Condensation with alcoholic ammonia or with amines to yield alkylamines.

$$C_nH_{2n+1}X + NH_3 \longrightarrow C_nH_{2n+1}NH_2 + HX.$$

(4) Condensation with hydrocarbons, or certain derivatives of hydrocarbons, under the influence of Friedel-Crafts condensing agents to furnish alkylated derivatives; as for example:

$$C_nH_{2n+1}X + C_6H_6 \xrightarrow{AlCl_3} C_nH_{2n+1}C_6H_5 + HX.$$

The use of trialkyl or triaralkyl borates has been proposed in place of the halides generally employed in this type of condensation.[1]

(5) Replacement of halogen by certain acid radicals, such as —CN, —SH, and others through interaction with salts of these acids.

$$C_nH_{2n+1}X + KCN \longrightarrow C_nH_{2n+1}CN + KX$$

$$C_nH_{2n+1}X + KSH \longrightarrow C_nH_{2n+1}SH + KX$$

$$C_nH_{2n+1}X + AgNO_2 \longrightarrow C_nH_{2n+1}NO_2 + AgX$$

(6) Interaction with metallic magnesium to yield Grignard compounds capable of being utilized in numerous syntheses.

$$C_nH_{2n+1}X + Mg \longrightarrow C_nH_{2n+1}MgX.$$

An industrial application of the Grignard synthesis is the preparation of lead tetraethyl from the halogen derivatives of ethane. In one procedure ethyl chloride, dissolved in ethyl ether, is treated with lead chloride and magnesium turnings. After treatment with water and sodium hydroxide, the ether is removed by distillation, and the lead tetraethyl recovered by steam-distillation.[1a]

The most technically important reactions of the alkyl chlorides, namely hydrolysis to alcohols and interaction with metallic salts to furnish esters, have already been discussed in detail in Chapter 33.

THE DECOMPOSITION OF ALKYL HALIDES INTO OLEFINS

The alkyl halides are decomposed to yield olefins and hydrogen halides according to the reaction, $C_nH_{2n+1}X \rightarrow C_nH_{2n} + HX$, by the action of chemical reagents, such as alkalies or alkali salts of organic acids, as well as by the action of heat with or without catalytic influence. The production of olefins during the hydrolysis of alkyl halides by alkalies, as in the production of alcohols, occurs most readily in the case of the tertiary halides and least so in the case of the primary compounds. Dechlorination of the chlorinated hydrocarbon may be effected by the action of hot alkalies in aqueous or alcoholic solutions but the reaction yields ethers and alcohols as well as olefinic hydrocarbons.[2] Organic bases can be used also for dechlorination, for example, Fortey[3] was able to obtain cyclohexene by heating chlorocyclohexane with quinoline.

The production of olefins from alkyl halides under the influence of heat, with or without catalysts, is a reversible process in certain instances such as ethylene, propylene and tertiary olefins, in which the point of equilibrium in the reaction, $C_nH_{2n+1}X \rightleftarrows C_nH_{2n} + HX$, is displaced towards the right-hand side of the equation with rising temperature.[3a] Accordingly low temperatures favor the production of alkyl halides from olefins,[4] while higher temperatures favor the production of olefins from these halides. In general the alkyl iodides are most readily decomposed by heat (especially the tertiary iodides) and the chlorides least so. Methyl chloride is the most resistant of the alkyl halides to thermal decomposition but pyrolysis is quite noticeable at about 500° C. The products consist of hydrogen chloride, carbon, methane, and other hydrocarbon gases.[5] In contrast to the thermostability of methyl chloride, the compound methyl iodide, though the most stable alkyl iodide, undergoes some decomposition at about 270° C. yielding methane, ethylene, and iodine.[6]

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[1] Kaufmann, French Patent 720,034, 1931; *Chem. Abs.*, 1932, 26, 3803.

[1a] Daudt, U. S. Patent 1,798,593, March 31, 1931; assigned to E. I. duPont de Nemours and Co., Inc.

[2] Nef, *Ann.*, 1899, 309, 128; 1901, 318, 1.

[3] *J.C.S.*, 1898, 73, 941.

Ethyl chloride was found by Nef[7] to be decomposed at 510° to 530° C. in the presence of pumice to yield 55 per cent of ethylene, while at 560° to 600° C. 76.8 per cent of ethylene was produced. The marked catalytic influence of the chlorides of the divalent elements (nickel, cobalt, iron, cadmium, lead, and especially barium) on the decomposition of alkyl chlorides into olefins at temperatures as low as 260° C. was shown by the work of Sabatier and Mailhe.[8] Brooks[9] obtained quantitative yields of ethylene and propylene from ethyl and propyl chlorides respectively by the catalytic influence of barium chloride on pumice at 400° to 450° C.

The decomposition of the propyl chlorides into propylene and hydrogen chloride has been studied by a number of workers. Sabatier and Mailhe[8] obtained good results with barium chloride, or other divalent metallic chlorides, at 260° C., but the catalyst tended to become gray in color because of the simultaneous polymerization of some of the olefins. According to Senderens,[10] alumina is an excellent catalyst for the decomposition of propyl and isobutyl chlorides at temperatures above 250° C. For example, propyl and isobutyl chlorides gave, with alumina as catalyst, at 350° C. a 97 per cent yield of propylene and 95 per cent of isobutylene, respectively.

The pyrolysis of 1- and of 2-chlorobutane both in the absence and in the presence of a catalyst (calcium chloride) has been investigated by Weston and Hass.[11] In the absence of catalysts the decompositions of 1-chlorobutane (at 550° C.) and of 2-chlorobutane (at 500° C.) were found to be homogeneous gaseous reactions. 1-Chlorobutane yielded butene-1 as the only product, while 2-chlorobutane on decomposition yielded a mixture of butene-1, *cis*-butene-2 and *trans*-butene-2. At 450° C. and in the presence of the catalyst both of the chlorobutanes were decomposed into mixtures of principally the *cis*- and *trans*-butene-2, together with a small proportion of butene-1. At still lower temperatures (400° C. and 250° C.) almost no butene-1 was formed by the decomposition of 2-chlorobutane. With both of the chlorobutanes the percentage of decomposition was observed to increase with increasing times of exposure to the heated reaction zone. It was not determined whether the butenes rearranged in the presence of the catalyst or whether the catalyst induced decomposition with formation of the two butene-2 compounds directly from the chlorobutanes.

[3a] The kinetics of the decomposition of alkyl halides in the gas phase at 300° to 400° C. has been studied by Lessig (*J. Phys. Chem.*, 1932, **36**, 2325; *Chem. Abs.*, 1932, **26**, 5000).

[4] An account of the production of alkyl halides from olefins is given in Chapter 12.

[5] Dumas and Peligot, *Ann. chim. phys.*, 1835, **58**, (2), 28.

[6] Kahan, *J.C.S.*, 1908, **93**, 132.

[7] *Ann.*, 1901, **318**, 14.

[8] *Compt. rend.*, 1904, **138**, 407; 1905, **141**, 238.

[9] *Chem. Met. Eng.*, 1920, **22**, 629.

[10] *Compt. rend.*, 1908, **146**, 1211; *Bull. soc. chim.*, 1908, **3**, (4), 827.

[11] *J.A.C.S.*, 1932, **54**, 3337.

As previously mentioned in Chapter 33, Ayres[12] observed the following percentage decomposition of various amyl chlorides in the liquid phase at 180° C.

	Decomposed per Min. at 180° C. Per Cent
Primary chlorides	0.08
Secondary chlorides	0.65
Tertiary chloride	3.70

It is evident that the decomposition of the tertiary chloride is considerable at 180° C., though it is inappreciable at 100° C. According to Ayres the formation of amylenes from the amyl chlorides is not accelerated by moisture, caustic soda, amyl alcohols or fatty acids and the only amylene formed in an alkaline hydrolysis of an amyl chloride is that derived from the purely thermal decomposition of the chloride.

Faragher and Garner[13] studied the catalytic production of olefins from chlorinated hexane, isohexane, cyclohexane, and heptane. They found that the stability of the monochloro-derivatives at a given temperature decreased with increasing molecular weight, at least up to about 7 carbon atoms in the chain. The following catalysts were tried at temperatures of 150° C. and over: alumina, unglazed porcelain, and porcelain impregnated with barium chloride. Of these catalysts, alumina was the most efficient, but all three lost their activity rapidly because of the poisoning by the decomposition of the hydrocarbons. The employment of temperatures higher than 200° C. resulted in a more complete decomposition of the chloro-compound, a fact which is well illustrated in Table 139, which gives experimental results showing the iodine numbers of products from the catalytic decomposition of chloroheptane at temperatures of 150° C. to 400° C. in the presence of various contact materials. The theoretical iodine number for a heptene is 260.

TABLE 139.—*Iodine Numbers of Condensates from the Catalytic Decomposition of Chloroheptane.*

Temp. ° C.	Unglazed Porcelain	Alumina	Unglazed Porcelain and Barium Chloride	Pyrex Glass
150	100	—	—	—
200	127	198	178	52.5
250	192	238	187	64
300	260	254	170	83
400	265	250	180	181

The condensates obtained in the experiments of Faragher and Garner readily yielded fairly pure olefins on fractionation. This method of removing hydrogen chloride from a chloro-compound is recommended by these workers. No indications of the extent of isomerization occurring during the reaction are given but, at the higher temperatures at any rate, considerable rearrangement must have occurred. Moreover, the rapid poisoning of the catalyst is an obvious disadvantage of this and similar methods. For the production of trimethylethylene from isoamyl chloride, isoprene from chloroisoamylene, and butadiene from dichlorobutane, Müller-Cunradi and Ober[13a] suggested a catalyst of titanium dioxide at 300° to 500° C. under atmospheric or reduced pressure.

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[12] *Ind. Eng. Chem.*, 1929, 21, 899.
[13] *J.A.C.S.*, 1921, 43, 1715.
[13a] German Patent 565,160, 1930; assigned to I. G. Farbenindustrie A.-G., *Chem. Abs.*, 1933, 27, 992.

The observation of Faragher and Garner that the tendency of decomposition of the alkyl chlorides increases with increasing molecular weight is in agreement with the results of Schaarschmidt and Thiele [14] on the production of fatty acids from paraffin. It was found that chlorine can be quantitatively removed from (mono-) chloro-derivatives of paraffin merely by heating the chloroparaffin at about 300° C. The resulting olefin, however, possessed a much lower iodine value than that obtained by the action of alcoholic alkali, a result indicating that the olefin, initially produced, had undergone partial cyclicization. Similar observations were made by Gardner and Bielouss [15] on the chlorinated paraffins of 17 or more carbon atoms. These chloro-compounds could be completely dechlorinated by heating to about 250° C. without the aid of catalysts but the products showed much lower iodine numbers than required by theory, again showing that partial transformation of the olefins to cyclic hydrocarbons had taken place under the influence of heat. The work of Gardner and Bielouss was directed toward the application of the olefinic compounds produced by thermal decomposition of chlorinated high molecular weight paraffins, as drying oils. The reactions of these hydrocarbons with several reagents were also investigated. At temperatures ranging from —5° to +20° C. sulphuric acid combined with a small proportion of the unsaturated hydrocarbons in the product to yield alkylsulphuric acids, which could be hydrolyzed to alcohols. The principal action of sulphuric acid was the almost complete polymerization of the unsaturated hydrocarbons. With sulphur monochloride, in amounts varying from 10 to 30 per cent of the hydrocarbons, the formation of hard and brittle products took place. When treated with this same reagent (sulphur monochloride) but in the presence of 10 to 15 per cent tung oil, rubber-like substances were obtained, which were similar in appearance to some of the so-called vulcanized oils. The use of concentrated nitric acid resulted in the polymerization of these hydrocarbons.

While some unsaturated hydrocarbons can be esterified by organic acids, Gardner and Bielouss failed to obtain such esters from their product on treatment with either acetic acid for 8 to 10 hours at 120° to 130° C. or with abietic acid for 6 to 8 hours at 200° C.

Gardner [16] has also described a procedure for the dechlorination of chlorinated petroleum products by heating the chlorinated oil to temperatures of 210° C. or higher in the presence of high-boiling materials, such as soya-bean oil, castor oil, and paraffin wax. The unsaturated hydrocarbons may be recovered by vacuum distillation and are said to be useful in the manufacture of varnishes.

According to Gardner,[17] these unsaturated hydrocarbons, or dechlorinated oils, may be used together with sulphur and rubber to produce tough molded articles, which can be vulcanized. The addition of fillers or pigments, such as zinc oxide, barium sulphate or lampblack, can be made also. Tire-treads, shoe soles, laminated waterproof fabrics or coatings for paper, are examples of the types of uses. Shiffler, Holm and Miller [17a] dechlorinated distillates containing combined chlorine formed as a result of cracking with aluminum chloride, by heating them at 150° C. under pressure in the presence of ferrous sulphide or calcium oxide.

Polychlorinated paraffin hydrocarbons may be converted to either saturated

[14] *Ber.*, 1920, **53**, 2128.

[15] *Ind. Eng. Chem.*, 1922, **14**, 619; Bielouss, U. S. Patent 1,384,423, July 12, 1921; *Chem. Abs.*, 1921, **15**, 3758.

[16] U. S. Patent 1,484,018, Feb. 19, 1924; *J.S.C.I.*, 1924, **43**, 435B.

[17] U. S. Patent 1,446,039, Feb. 20, 1923; *J.S.C.I.*, 1923, **42**, 366A.

[17a] U. S. Patent 1,869,781, Aug. 2, 1932; assigned to Standard Oil Co. of California; *Brit. Chem. Abs.* **B**, 1933, 499.

or unsaturated products by means of alkalies. When the halogenated hydrocarbons, containing more than 8 carbon atoms and not more than 9 chlorine atoms per molecule, are boiled under a reflux apparatus with solutions of sodium hydroxide or carbonate, dechlorination is effected with the formation of saturated substances. In this procedure catalysts such as copper salts or the oxides or hydroxides of iron or zinc may be employed. On the other hand, by heating chlorinated hydrocarbons with milk of lime under pressure at 150° to 160° C. unsaturated hydrocarbons possessing the characteristics of drying oils are obtained.[18]

If in place of refluxing the chlorinated hydrocarbons with solutions of sodium hydroxide or carbonate the reaction is carried out under pressure, then light-colored viscous oils are the result. These oils are probably unsaturated monohydric alcohols and may still contain halogens.[19]

Monochloro-derivatives of the Cycloparaffins. Faragher and Garner reported that monochloro-cyclohexane was much more readily decomposed than the alkyl chlorides of 6 and 7 carbon atoms and this rule also applies to the higher chlorinated derivatives. The ease with which the chlorinated cycloparaffins decompose to yield cyclic olefins and hydrochloric acid was employed by Thiele[20] in making drying oils from kerosene containing considerable proportions of cycloparaffins. Chlorinated kerosene is acidified with acetic acid and then treated with metallic zinc. The cleavage of hydrogen chloride from various mono- and dichlorocyclohexanes by the use of catalysts, such as barium chloride or alumina, has been proposed by Schmidt, Hochschwender and Eichler.[21]

ISOMERIZATION PHENOMENA AMONG ALKYL HALIDES

Many alkyl halides, when heated either in the liquid or gaseous phases, exhibit a marked tendency to isomerize to a more stable isomer. The general trend appears to be for primary halides to isomerize to secondary which in turn possess a disposition to be transformed to tertiary compounds whenever possible. There is little doubt that this isomerization reaction takes place by the intermediate production of an olefin,[22] so that the conversion of n-propyl bromide into isopropyl bromide may be represented as follows:

$$\mathrm{CH_3CH_2CH_2Br} \longrightarrow (\mathrm{CH_3CH{=}CH_2 + HBr}) \longrightarrow \mathrm{CH_3CHBrCH_3}$$

According to Brunel,[23] n-propyl bromide when heated in the liquid phase for 1 hour at 262° C. is converted to the extent of about 22 per cent into the iso-form, while in the gaseous phase at the same temperature a conversion of over 34 per cent was observed after 2 hours. The reverse process, conversion of isopropyl bromide into the n-bromide, takes place at 260° C. though very much more slowly. In the gaseous phase at 360° C. an equilibrium is ultimately set up in which the ratio of iso- to n-bromide is 73:27; quantities of hydrogen bromide and propylene are also present.[24] In a similar way, isobutyl bromide may be isomerized to the tertiary bromide to the extent of 72 to 74 per cent by heating at 140° C.

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[18] I. G. Farbenindustrie A.-G., British Patents 372,784 and 372,785, 1931; *Brit. Chem. Abs.* **B**, 1932, 714.

[19] I. G. Farbenindustrie A.-G., British Patent 343,948, 1929; *Brit. Chem. Abs.* **B**, 1931, 578.

[20] U. S. Patent 1,254,866, Jan. 29, 1918; *Chem. Abs.*, 1918, **12**, 769.

[21] U. S. Patent 1,221,382, Apr. 3, 1917; *Chem. Abs.*, 1917, **11**, 1885; British Patent 5,429, 1912; *J. S. C. I.*, 1913, **32**, 47; German Patent 254,473, 1911; *Chem. Abs.*, 1913, **7**, 1266; German Patent 255,538, 1912; *Chem. Abs.*, 1913, **7**, 1587; all patents assigned to Badische Anilin- und Soda-Fabrik.

[22] Lucas and Jameson, *J.A.C.S.*, 1924, **46**, 2479.

[23] *Ann.*, 1911, **384**, 245.

[24] Brunel and Rafsky, *Science*, 1924, **60**, 23.

for 15 hours,[25] while the tertiary bromide may be partially reconverted to the isobutyl bromide by heating to temperatures of 180°-260° C. for several hours. At 237° C. in the liquid phase the equilibrium appears to correspond to a mixture of 73 per cent tertiary and 27 per cent of isobutyl bromides, but in the gaseous phase at 280° C. the equilibrium mixture contains 90 to 91 per cent of the tertiary form.[26]

A number of transformations of amyl bromides have been studied in some detail by Michael and Leupold,[27] who found that the tertiary compound is the most stable variety. Nevertheless tertiary amyl bromide, when heated in the liquid state at 184° C. for 30 minutes, underwent a 7 per cent conversion to active amyl bromide (1-bromo-2-methylbutane) and about 12 per cent to 3-bromo-2-methylbutane, so that here again an equilibrium appears to exist in which the tertiary compound is always in excess.

REACTION OF MONOCHLORINATED PARAFFINS AND CYCLOPARAFFINS WITH AMMONIA AND AMINES

The primary and secondary alkyl halides may be condensed with ammonia (and amines) to furnish alkylamines, but this condensation is not applicable to tertiary halides which yield olefins on treatment with ammonia. The reaction with ammonia, which is usually effected by heating the halide with an alcoholic ammonia solution, leads to the production of mono-, di-, and tri-alkylamines as well as of quaternary ammonium salts, though conditions can be often arranged so that a preponderance of one product is obtained. By heating an alcoholic ammonia solution of ethyl chloride in sealed tubes at 100° C., Groves[28] noted the formation of ethylamine together with some diethylamine and triethylamine. The reaction was further investigated by Hofmann,[29] who showed that, besides the three amines already noted, tetraethylammonium chloride is also formed under certain conditions. The yields of the various products depend mainly upon the relative proportions of the reactants. The several stages of the condensation between ethyl chloride and ammonia may be summarized by the following reactions:

$$C_2H_5Cl + NH_3 \longrightarrow C_2H_5NH_2 + HCl$$
$$C_2H_5Cl + C_2H_5NH_2 \longrightarrow (C_2H_5)_2NH + HCl$$
$$C_2H_5Cl + (C_2H_5)_2NH \longrightarrow (C_2H_5)_3N + HCl$$
$$C_2H_5Cl + (C_2H_5)_3N \longrightarrow (C_2H_5)_4NCl$$

According to Henning,[30] the ethylation of ammonia and other amines by means of ethyl chloride can readily be effected by heating the reactants together for 4 hours in an autoclave at 100° C. and under about 150 lbs. pressure.

Examples of the alkylation of ammonia by means of alkyl chlorides are very numerous. Malbot[31] reported the formation of mono- and di-isopropylamines by heating isopropyl chloride with ammonia. When alkyl halides are treated with a solution of sodamide in liquid ammonia, two concurrent reactions take place resulting in the formation of alkylamines and olefin hydrocarbons. These processes are exemplified by the case of the condensation of ethyl chloride with sodamide, which may be represented in the following manner:[32]

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[25] Michael and Leupold, *Ann.*, 1911, 379, 263.
[26] Brunel, *Ber.*, 1911, 44, 1000.
[27] Michael and Leupold, *Ann.*, 1911, 379, 263.
[28] *J.C.S.*, 1860, 13, 331.
[29] *Ber.*, 1870, 3, 109.
[30] *J.S.C.I.*, 1920, 39, 1 T; *cf.* Callan, *Chem. Age (London)*, 1920, 3, 557.
[31] Malbot and Malbot, *Bull. soc. chim.*, 1890, (3) 4, 340, 632; *Chem. Soc. Abs.*, 1891, 60, 413.

$$C_2H_5Cl + NH_2Na \longrightarrow NaCl + C_2H_5NH_2$$

and

$$C_2H_5Cl + NH_2Na \longrightarrow NaCl + NH_3 + C_2H_4$$

On the other hand, when alkyl chlorides are treated at —40° C. with ammonia and an alkali metal (i.e., a metallic ammonium compound) primary amines and paraffin hydrocarbons are formed according to the typical reactions:[33]

$$CH_3Cl + 2NH_3Na \longrightarrow CH_4 + NH_2Na + NaCl + NH_3$$
$$RCl + NH_3Na \longrightarrow RNH_2 + NaCl$$

The alkylation of aliphatic and aromatic amines can similarly be effected by heating an alkyl halide with the amine. The condensation of n-propyl chloride with ethylamine to furnish ethylpropylamine and ethyldipropylamine has been described by Comanducci and Arena.[34] The alkylation of aromatic amines by means of alkyl chlorides is exemplified by the condensation of 1-chlorobutane with o- and p-toluidines, a reaction investigated by Reilly and Hickinbottom.[35]

Groggins and Stirton[35a] studied the effect of catalysts on the reaction of aqueous ammonia with halogenated compounds and observed that the activity of the catalyst depends upon the type of organic compound and that a small proportion of water catalyzes the reaction. For example, ethylene dichloride can be reacted with aqueous ammonia at 110° C. to form ethylenediamine without the use of a catalyst, though copper, or some other metal following hydrogen in the electrochemical series, is necessary in the reaction of ammonia with compounds containing a halogen attached to the phenyl nucleus, such as chlorobenzene, 4-chloro-2-phenylanthraquinone, and chlorobenzoylbenzoic acids. They also noted that the addition of ammonium nitrate or oxidants, such as potassium chlorate, to the copper compounds increased the yield and purity of the resulting amine. This was especially true in the amination of compounds containing the halogen attached to the phenyl nucleus. Contrary to the conclusions of Hale and Britton[35b] in their work on aniline, Groggins and Stirton found that the presence of metallic copper is not necessary when copper compounds are used as catalysts, nor is it advantageous to keep the copper catalyst in a reduced state.

That ammonolysis is brought about by the activity of ammonia and not by the base ammonium hydroxide is concluded by Groggins and Stirton on the basis of the following observations: Ammonolysis may be carried out in the vapor phase with anhydrous ammonia or in the liquid phase with anhydrous ammonia dissolved in an inert diluent. The properties of the system, ammonia-water, are those of a typical mixture. No ammonolysis takes place when equivalent amounts of ammonium salts are substituted for the ammonia. Colorimetric studies in sealed glass tubes show that the p_H of aqueous ammonia decreases with rising temperature and that this decrease is more rapid when ammonium salts are added.

Salts of diguanidine derivatives of the higher molecular weight paraffin hydrocarbons may be prepared by the reaction between α,β-dihalogen derivatives of these hydrocarbons and guanidine in warm alcohol solutions.[36]

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[32] Chablay, *Compt. rend.*, 1913, **156**, 327; *Chem. Zentr.*, 1913, **1**, 1003.
[33] Lebeau, *Compt. rend.*, 1905, **140**, 1042, 1264.
[34] *Giro. Farm. Chim.*, 1907, **56**, 385; *Chem. Zentr.*, 1907, **2**, 1396.
[35] *J.C.S.*, 1918, **113**, 974.
[35a] *Ind. Eng. Chem.*, 1933, **25**, 42, 169, 274.
[35b] U. S. Patent 1,607,824, Nov. 23, 1926; *Brit. Chem. Abs.* **B**, 1927, 101; Reissue 17,280, Apr. 23, 1929; assigned to Dow Chemical Co.

The manufacture of nitrogen-containing compounds of the higher paraffins is described by the I. G. Farbenindustrie A.-G.[37] Halogenated derivatives of the paraffin hydrocarbons of more than 8 carbon atoms are heated with ammonia in aqueous or alcoholic solution, or with agents yielding ammonia, e.g., ammonium carbonate or urea, with or without the addition of copper compounds as catalysts. The heating is best carried out under increased pressure. These compounds can be sulphonated to give emulsifying agents.[37a]

Substances which may be employed as wetting, cleansing, tanning or dispersing agents can be prepared by the condensation of halogenated paraffin hydrocarbons, containing more than nine carbon atoms, with amines or substituted amines.[38] For example, paraffin wax (m.p. 46° to 50° C.) is chlorinated until a 25 per cent increase in weight is obtained. The chlorinated hydrocarbon is made to react at 180° C. with 2-hydroxyethylamine, and the resulting product is esterified at 50° to 60° C. with chlorosulphonic acid. This procedure yields a substance which may be used as a wetting agent. A leather-softening agent is obtained as the result of the reaction between chlorinated brown-coal tar oil (b.p. 200° to 300° C.) and n-butylamine, while chlorinated paraffin oil (b.p. 150° to 300° C.) and p-aminophenol unite to give a dispersing agent.

The amines generally are stronger bases than ammonia, and readily form salts with both organic and inorganic acids. This is particularly true of the alkylamines derived from paraffin hydrocarbons having about 6 or less carbon atoms in the molecule. As a rule the solubility of such amines in water decreases with the number of alkyl groups attached to the nitrogen atom. For a given series of amines having the same hydrocarbon radical the primary amine is the most soluble, the secondary less so, and the tertiary amine the least soluble. In addition to being fairly strong bases the amines are also solvents for many organic substances.[39]

Production of Ethers from Monochlorinated Paraffins

Alkyl halides can be condensed with sodium alcoholates or alkali salts of phenols to form ethers, the reactions being:

$$RX + NaOC_nH_{2n+1} \longrightarrow ROC_nH_{2n+1} + NaX$$
$$RX + NaOC_6H_5 \longrightarrow ROC_6H_5 + NaX$$

The second reaction, namely, the formation of arylalkyl ethers, is of great industrial importance in the dye industry and is effected more readily than the first reaction. In general, it is sufficient to heat the alkyl halide with an alkaline solution of the phenol under pressure. Ethyl chloride is used extensively for the ethylation of certain phenols employed in the preparation of hydroxyazo dyes whereby the fastness of these dyes to alkalies is greatly increased. An example of a dye which is stabilized to alkalies by the introduction of an ethyl group in a phenolic OH group is Chrysophenine G, which is obtained by the condensation of diazotized diaminostilbene-sulphonic acid with two molecules of phenetol

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[36] Von Godin, German Patent 518,407, 1928; *Chem. Abs.*, 1931, **25**, 2439.

[37] British Patent 339,962, 1929; *Brit. Chem. Abs.* **B**, 1931, 194.

[37a] I. G. Farbenindustrie A.-G., British Patent 383,736, 1932; *Chem. Abs.*, 1933, **27**, 4390.

[38] I. G. Farbenindustrie A.-G., British Patent 359,001, 1930; *Brit. Chem. Abs.* **B**, 1932, 173.

[39] For the solubilities of a large number of organic compounds in various alkylamines, see Bergstrom, Gilkey and Lung, *Ind. Eng. Chem.*, 1932, **24**, 57.

(ethyl phenyl ether). According to Henning,[40] most industrial ethylations of hydroxylic compounds by means of ethyl chloride can be accomplished by heating in an autoclave under 160 lbs. pressure at about 100° C., but this has been contested by Callan.[41]

Dispersing, emulsifying or softening agents may be obtained by the sulphonation or halogenation of the ethers derived from chlorinated high molecular weight paraffin hydrocarbons, that is, those containing 9 or more carbon atoms per molecule, and polyhydric alcohols or phenols or naphthols.[42] As an example, chlorinated petroleum hydrocarbons may be etherized with the monosodium derivative of ethylene glycol and the resulting ether, which contains a hydroxyl group, then esterified with chlorosulphonic acid at 40° to 50° C.

The reaction between alkyl chlorides and alkali phenoxides is capable of extension to the higher members of the series of alkyl chlorides, so that high molecular weight ethers, some of which may have industrial applications, can be produced. Bosshard and Strauss [43] described the production of a phenoxyparaffin, a soap-like mass of melting point 60° C., by heating a monochlorinated solid paraffin with phenol, potassium carbonate, and a solvent under reflux. This phenoxyparaffin can be sulphonated to a semi-solid fat-like substance soluble in water which can be used in the tanning industry. The production of α- or β-naphthoxyparaffins, from the chloroparaffin and alkaline α- or β-naphthols respectively, can be similarly effected.

Carbohydrate ethers have been prepared by reacting alkyl halides, such as ethyl chloride, with a mixture of cellulose and a metallic hydroxide in suspension in an organic liquid.[43a]

NUCLEAR ALKYLATION OF AROMATIC COMPOUNDS BY MEANS OF ALKYL HALIDES

The alkyl chlorides may be used for the introduction of alkyl groups into the aromatic nucleus. Not only may aromatic hydrocarbons be readily alkylated by treatment with an alkyl chloride in the presence of a suitable condensing agent, but the process can also be extended to the alkylation of phenols, aromatic ketones, and other compounds. The condensing agent most frequently employed is anhydrous aluminum chloride but other anhydrous metallic halides can also be employed in some cases. These processes belong to the series of synthetic reactions usually designated by the names of their discoverers, Friedel and Crafts.[44] The reactions proceed more readily in the case of the bromides than with the chlorides while tertiary compounds appear to undergo this process with particular ease. A large number of nitrated tertiary butyl aromatic compounds having strong musk-like odors, were prepared by the aid of this reaction.[45]

An important peculiarity of this process of alkylating aromatic hydrocarbons is that the alkyl group frequently undergoes an isomerization reaction during the process of alkylation and presumably under the powerful catalytic influence of the anhydrous metallic halide. Thus n-propyl bromide reacts with benzene to furnish mainly an isopropylbenzene, while n-butyl bromide condenses to furnish a secondary butyl product. Treatment of benzene with (primary) isobutyl chloride in the presence of aluminum chloride leads to the production of tertiary butylbenzene together with some isobutylbenzene.[46] Numerous other examples of such isomerization phenomena during this condensation might be cited. Schmidt, Ernst and Lange[46a] formed alkylnaphthalenes by heating naphthalene with monochlorinated compounds, such as chloromethane or chloroethane at 160° to 180° C. under pressures as high as 45 atmospheres in the presence of zinc chloride or oxide.

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[40] *J.S.C.I.*, 1920, **39**, 1T.

[41] *Chem. Age* (*London*), 1920, **3**, 557.

[42] I. G. Farbenindustrie A.-G., British Patent 360,493, 1930; *Brit. Chem. Abs.* **B**, 1932, 252. *Cf.* French Patent 709,626, 1931, *Chem. Abs.*, 1932, **26**, 1403.

[43] German Patent 344,878, 1917; assigned to Elektrochemische Werke G.m.b.H.; *Chem. Abs.*, 1923, **17**, 1243.

[43a] Liebster, French Patent 730,038, 1931; *Chem. Abs.*, 1933, **27**, 305.

[44] For an account of Friedel-Crafts syntheses see Kränzlein, "Aluminiumchlorid in der organische Chemie," Verlag Chemie, Berlin, **1932**.

[45] Baur, *Ber.*, 1891, **24**, 2832; Baur-Thurgau, *Ber.*, 1898, **31**, 1344; Baur-Thurgau and Bischler, *Ber.*, 1899, **32**, 3647; see also Chapter 17 (footnote 43), in which a number of patents are listed.

Phenols may similarly be alkylated by treatment with an alkyl chloride in the presence of anhydrous aluminum chloride. In this way 4-tertiary butyl-β-naphthol may be prepared from β-naphthol and tertiary butyl chloride.[47] The alkylation of phenols by alkyl halides in the presence of anhydrous ferric chloride has been studied by a number of investigators.[47a] Linner[47b] prepared p-tertiary-butylphenol by passing isobutylene through a solution of phenol in carbon tetrachloride containing aluminum chloride in suspension and a small proportion of tertiary butyl chloride. The reaction is initiated by the alkyl chloride and the hydrogen chloride liberated combines with the isobutylene to form additional alkyl chloride to continue the reaction. 4-Hydroxytetraphenylmethane results by the reaction of triphenylmethyl chloride and phenol in the presence of aluminum chloride.[47c]

The alkylation of aromatic hydrocarbons by means of the higher alkyl chlorides has led to the use of these chlorides in the production of synthetic lubricating oils of value for blending with natural petroleum lubricants to lower their pour point. Thus a synthetic lubricating oil possessing these pour-reducing properties has been produced by condensing a monochlorinated paraffin wax with a solid aromatic hydrocarbon, such as naphthalene, at low temperatures and in the presence of aluminum chloride as a condensing agent.[48]

DOUBLE DECOMPOSITION OF SALTS OF INORGANIC ACIDS WITH ALKYL HALIDES

Production of Nitriles. The reaction of primary and secondary alkyl halides with metallic cyanides results in the formation of nitriles according to the reaction:

$$RX + MCN \longrightarrow RCN + MX$$

(M = monovalent element, such as Na, K, etc.)

The nitriles, so produced, may be made the starting point for a large number of syntheses of valuable organic chemicals, including aliphatic acids, amines, amides or alcohols. Despite the fact that the reaction has been known for many years, it is surprising to find that it has been very little studied. The reaction of a number of alkyl chlorides with potassium cyanide to yield nitriles by heating them in aqueous alcoholic solution was studied by Lieben and Rossi.[49] Adams and Marvel[50] succeeded in producing valeronitrile from butyl bromide and sodium cyanide under similar conditions.

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[46] Bödtker, *Bull. soc. chim.*, 1904, (3) **31**, 966; *Chem. Soc. Abs.*, 1904, **86** (1), 801.

[46a] U. S. Patent 1,879,912, Sept. 27, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 309.

[47] Koenigsberger, U. S. Patent 1,788,529, Jan. 13, 1931; *Chem. Abs.*, 1931, **25**, 974.

[47a] See Gurewitsch, *Ber.*, 1899, **32**, 2428.

[47b] U. S. Patent 1,892,990, Jan. 3, 1933; assigned to Beck, Koller and Co.; *Chem. Abs.*, 1933, **27**, 2319; Austrian Patent 124,281, 1931; *Chem. Abs.*, 1932, **26**, 735; French Patent 697,711, 1930; *Chem. Abs.*, 1931, **25**, 3013; both patents assigned to Soc. Reichhold, Flügger and Boecking.

[47c] Baeyer, *Ber.*, 1909, **42**, 2625; Busch and Knoll, *Ber.*, 1927, **60**, 2243; *Chem. Abs.*, 1928, **22**, 400.

[48] Davis, U. S. Patent 1,815,022, July 14, 1931; assigned to Standard Oil Development Co. For a description of the preparation and properties of this synthetic oil see Chapter 30.

[49] *Ann.*, 1871, **159**, 75.

[50] *J.A.C.S.*, 1920, **42**, 318.

Later Hass and Marshall[51] reported the synthesis of caproic acid by the hydrolysis of amyl cyanide. The optimum conditions for the production of the latter compound by the interaction of sodium cyanide and 1-chloropentane were determined. The best yields of amyl cyanide (68 to 70 per cent of the theoretical) were obtained by refluxing 1 mole of the chloride with a slight excess of sodium cyanide (1.1 moles) in aqueous ethanol solution for 48 hours or longer. A solvent consisting of 80 per cent ethanol and 20 per cent of water is suitable for this purpose. These yields were very greatly improved by the addition of sodium iodide to the reaction mixture, the increased yields being due to the intermediate production of the more reactive amyl iodide according to the scheme:

$$C_5H_{11}Cl + NaI \longrightarrow C_5H_{11}I + NaCl$$
$$C_5H_{11}I + NaCN \longrightarrow C_5H_{11}CN + NaI$$

By refluxing an equimolecular mixture of amyl chloride and sodium iodide with a 10 per cent excess of sodium cyanide in 80 per cent ethanol-water for 24 hours, a 90 per cent yield of crude n-amyl cyanide was obtained.

The hydrolysis of n-amyl cyanide was readily effected by warming it with an equimolecular amount of 67 per cent sulphuric acid for 30 minutes when caproic acid was obtained in excellent yield.[52] Aliphatic nitriles are said to be readily hydrolyzed to acids by treatment with 90 per cent phosphoric acid at 150° to 220° C.[53]

On attempting to apply their method for the preparation of nitriles to the secondary and tertiary amyl halides, Hass and Marshall found that the secondary amyl chlorides and bromides gave comparatively low yields of nitriles (about 30 per cent), while the tertiary chlorides or bromides gave no nitriles whatever.

This method of nitrile production can be applied to other primary alkyl chlorides with excellent yields. In the case of the lower boiling chlorides, such as butyl chloride, it is best to use superatmospheric pressure, for which purpose iron autoclaves are quite suitable.

Alkyl chlorides may be condensed with alkali hydrosulphides to yield mercaptans; with alkali sulphides to furnish sulphides or thioethers; and with a number of other metallic salts of various acids to yield the corresponding alkyl esters. Generally the reaction is more difficult to effect in the case of the chlorides than with the other halides, and in the laboratory the more reactive iodides are most frequently employed for such syntheses.

Keller[53a] suggested the preparation of sulphurized hydrocarbon derivatives by reacting halogenated higher aliphatic hydrocarbons with hydrosulphides, sulphides or polysulphides, under such condition that the chlorine is replaced completely or only in part by sulphur-containing groups. For example, trichlorinated hard paraffin wax is heated with a potassium hydroxide solution of hydrogen sulphide under pressure at 140° C., the products being insecticides.

The manufacture of ethyl mercaptan from ethyl chloride has been carried out on a considerable scale. Ethyl mercaptan is employed as a raw material in the synthesis of *sulphonal*, a very widely used hypnotic drug. This synthesis is effected by condensing ethyl mercaptan and acetone together in the presence of a catalyst, such as zinc chloride, with the production of a mercaptol, which is readily oxidized to the corresponding sulphone, or sulphonal.[54] The series of reactions is represented as follows:

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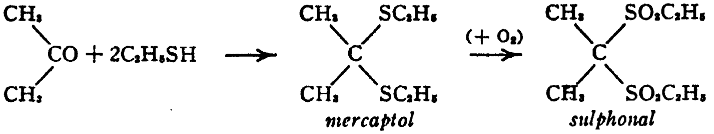
[51] *Ind. Eng. Chem.*, 1931, **23**, 352; *Chem. Abs.*, 1931, **25**, 2689.

[52] Caproic acid (pentane-1-carboxylic acid) is used in the preparation of *hexylylresorcinol* by condensation with resorcinol in the presence of zinc chloride; Dohme, U. S. Patent 1,649,669, Nov. 15, 1928; *Chem. Abs.*, 1928, **22**, 434. Reduction of this compound yields the well-known pharmaceutical product *hexylresorcinol;* Dohme, U. S. Patent 1,649,667, Nov. 15, 1927; *Chem. Abs.*, 1928, **22**, 434.

[53] I. G. Farbenindustrie A.-G., British Patent 339,235, 1929; *Brit. Chem. Abs.* **B**, 1931, 289.

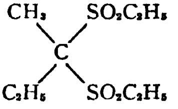
[53a] German Patent 557,245, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 310.

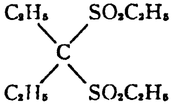
$$C_2H_5Cl + KSH \longrightarrow \underset{\textit{ethyl mercaptan}}{C_2H_5SH} + KCl$$



mercaptol *sulphonal*

Two other drugs of the same class may also be synthesized from ethyl mercaptan, namely trional and tetronal, having the following structural formulas:


trional


tetronal

Reaction of the Alkyl Chlorides with Magnesium

When alkyl halides are treated in anhydrous ethereal solution with pure magnesium ribbon direct combination takes place with the production of magnesium alkyl halide, the so-called Grignard reagent. These magnesium compounds are of great value in organic syntheses since they readily combine with a number of substances such as aldehydes, ketones, carbon dioxide and many others with the formation of new products. On a laboratory scale the more reactive alkyl magnesium iodides are generally employed, and little use has been made of the chlorides. However, the action of metallic magnesium on a few alkyl chlorides has been investigated. For example, tertiary butyl chloride readily combines with magnesium at 5° to 15° C. to yield a Grignard compound but at a higher temperature there is a tendency for decomposition to occur with the formation of isobutylene and isobutane, according to the reaction:[55]

$$2C_4H_9Cl + Mg \longrightarrow MgCl_2 + C_4H_{10} + C_4H_8$$

This disruptive process is even more pronounced at much higher temperatures. When isobutyl chloride is heated with magnesium for several hours at 260° C., the products consist of hydrogen, diisobutyl and a solid material.[56] It appears, however, that stable Grignard compounds can be prepared from alkyl chlorides in dry ethereal solution in the presence of a catalyst such as iodine or magnesium iodide. Schmalfuss[57] reported the preparation of a reactive Grignard reagent by passing gaseous methyl chloride into dry boiling ether containing finely divided magnesium and one or more catalysts. Organo-magnesium compounds may likewise be prepared from chlorinated aromatic hydrocarbons. For example, a Grignard compound results on heating magnesium with chlorobenzene to 160° to 170° C. Such products condense with ethylene oxide, ethylene chlorohydrin, ketones, aldehydes, or esters, to yield alcohols. The compound mentioned condenses with ethylene oxide to form β-phenyl alcohol.[57a]

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[54] Baumann, *Ber.*, 1886, **19**, 2805.
[55] Bouveault, *Compt. rend.*, 1904, **138**, 1108.
[56] Spencer and Crewdson, *J.C.S.*, 1908, **93**, 1821.
[57] German Patent 374,368, 1922; *J.S.C.I.*, 1923, **42**, 1202A.

The reaction of isopropyl magnesium bromide and allyl bromide yields, according to Risseghem,[57b] a mixture of 4-methyl-1-pentene and a more volatile product.

Grignard compounds are of little value industrially because of their high cost. However, Zelinski[58] has described a process of preparing the higher fatty acids by decomposing the Grignard compounds of higher monochlorinated hydrocarbons with carbon dioxide. The crude petroleum is chlorinated, the product is dissolved in anhydrous ether and the solution treated with magnesium. Solution of the magnesium is accelerated by the addition of a catalyst, such as iodine, methyl iodide, aluminum salts or hydrogen chloride. Into the cold ethereal Grignard reagent is passed a stream of carbon dioxide. The Grignard compound is thereby decomposed with the production of the magnesium salt of a fatty acid according to the reaction:

$$2RMgCl + 2CO_2 \longrightarrow (RCOO)_2Mg + MgCl_2,$$

where R represents a hydrocarbon residue. The fatty acids, so produced, are then liberated from the magnesium salts by treatment with dilute acid.[59] It is understood that this process, though of considerable scientific interest, is not economically practicable owing to the high cost of the magnesium which cannot be recovered as such. Nevertheless, in the production of some compounds, such as lead tetraethyl, organic metallohalides appear to be indispensable. Tetraethyl lead (tetraethyl plumbane) was prepared from (1) ethyl iodide and lead-sodium,[59a] (2) zinc diethyl and lead chloride,[59b] and (3) ethyl magnesium bromide and lead chloride.[59c] These methods have been modified later for application on an industrial scale. In several methods,[59d] lead-sodium alloys are heated together with ethyl halides, and in others[59e] magnesium ethyl halides are caused to react with lead chloride in the presence of a catalyst such as an alkyl iodide.[59f]

The Grignard reagents produced from the monohalogenated cycloparaffins exhibit a similar order of reactivity to those derived from straight chain components.

[57a] Shoruigin, Isagulyantz, Guseva, Poliakov, and Ossipova, French Patent 738,277, 1932; *Chem. Abs.*, 1933, **27**, 1638.

[57b] *Bull. soc. chim. Belg.*, 1933, **42**, 229; *Chem. Abs.*, 1933, **27**, 5052.

[58] French Patent 326,665, 1902; see also *Z. angew. Chem.*, 1903, **16**, 37.

[59] Colletas, *Les matieres grasses*, 1914, **7**, 4151; *J.S.C.I.*, 1914, **33**, 972.

[59a] Ghira, *Gazetta chim. ital.*, 1894, **24** (1), 44; *cf.* Cahours, *Ann.*, 1862, **122**, 65.

[59b] Buckton, *Ann.*, 1859, **109**, 222; *ibid.*, 1859, **112**, 226; Frankland and Lawrance, *J.C.S.*, 1879, **35**, 245.

[59c] Pfeiffer and Truskier, *Ber.*, 1904, **37**, 1127.

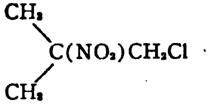
[59d] Midgley, U. S. Patent 1,622,228, Mar. 22, 1927; *Brit. Chem. Abs.* **B**, 1927, 349; British Patent 216,083, 1923; *J.S.C.I.*, 1925, **44**, 299B; Calingaert, U. S. Patent 1,622,233, Mar. 22, 1927; *Brit. Chem. Abs.* **B**, 1927, 428; all three patents assigned to General Motors Corp. Calcott and English, U. S. Patent 1,652,812, Dec. 13, 1927; *Brit. Chem. Abs.* **B**, 1928, 157; Calcott, Parmelee and Lorriman, U. S. Patent 1,664,021, Mar. 27, 1928; *Chem. Abs.*, 1928, **22**, 1677; British Patent 280,169, 1926; *Brit. Chem. Abs.* **B**, 1928, 893; French Patent 638,103, 1927; *Chem. Abs.*, 1929, **23**, 275; Calcott and Daudt, U. S. Patent 1,692,926, Nov. 27, 1928; *Brit. Chem. Abs.* **B**, 1929, 427; Amick, Downing and Parmelee, U. S. Patent 1,907,701, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3724; all patents assigned to E. I. duPont de Nemours and Co., Inc. Kraus and Callis, U. S. Patents 1,694,268, Dec. 4, 1928; *Brit. Chem. Abs.* **B**, 1929, 355; U. S. Patent 1,697,245, Jan. 1, 1929; *Brit. Chem. Abs.* **B**, 1929, 427; both patents assigned to Standard Oil Development Co.

[59e] Daudt, British Patent 279,106, 1927; *Brit. Chem. Abs.* **B**, 1928, 748; German Patent 533,779, 1927; *Chem. Abs.*, 1932, **26**, 738; both patents assigned to E. I. duPont de Nemours and Co., Inc.

[59f] An electrolytic method for the preparation of lead tetraethyl is described by Calingaert, U. S. Patent 1,539,297, May 26, 1925; assigned to General Motors Corp.; *J.S.C.I.*, 1925, **44**, 652B. The technical utilization of tetraethyl lead is discussed by Kalichevsky and Stagner, "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York **1933**, 283. The relation between aromatic, tetraethyl lead, and octane equivalents and their determination, and the characteristics of gasolines and the amounts of added tetraethyl lead are discussed by Sachanen and Tilicheyev, *Chemistry and Technology of Cracking*, translated by Boehtlingk, Brown and Steik, Chemical Catalog Co., Inc., New York, **1932**, 213-217.

OTHER REACTIONS OF THE ALKYL CHLORIDES AND MONOCHLORINATED CYCLOPARAFFINS

A number of alkyl chlorides can be readily nitrated by dilute nitric acid to furnish nitro-derivatives. For example, Konovalov prepared a chloronitroisobutane of the structure



$$(CH_3)_2C(NO_2)CH_2Cl$$

by nitration of isobutyl chloride at 70° to 100° C. The production of resinous or viscous oils, which may be used in varnish or pyroxylin compositions, has been described by Bielouss.[60] The procedure consists in chlorinating a mineral oil distillate of the paraffin type, specific gravity not less than 0.882, until about 20 per cent by weight of chlorine has been absorbed. The chlorinated oil is then nitrated, employing a mixture of nitric and sulphuric acids, at temperatures below 55° C.

According to Schrauth,[61] carboxylic acids may be made by fusing monochlorinated petroleum fractions with alkalies at 200° to 300° C. in such a manner as to avoid high pressure. The temperature is at first maintained at 200° to 230° C. and later raised to 300° C. The products obtained after 6 to 9 hours contain dry, odorless soaps soluble in hot water, with good lathering properties. The excess of alkali may be neutralized with mineral acid and the fatty acids extracted by means of steam or water. Hydrogen is evolved during the fusion. Under these conditions, cetyl chloride is said to be converted into palmitic acid. It appears probable that this reaction proceeds through the intermediate formation of an olefin which then combines with the alkali with the production of an alkali salt of a fatty acid and evolution of hydrogen. The series of reactions may be represented as follows:

$$RCH_2CH_2Cl \longrightarrow RCH{=}CH_2 + (HCl)$$
$$RCH{=}CH_2 + NaOH + H_2O \longrightarrow RCH_2COONa + 2H_2$$

Fatty acids are said to result also on heating olefins with water and alkali hydroxides, phenolates, naphthenates or other weak-acid salts, to 360° C. under pressures of about 46 atmospheres.[62] Sodium propionate may be formed from propylene in this manner, and from 2 liters of ethylene measured at 20° C. at 25.5 atmospheres were obtained 71.5 grams of acetic acid. In carrying out the process, for example, 200 grams of water, 65 grams of sodium hydroxide and 46 grams of ethylene are heated in an autoclave in the presence of an inert oil for 1 hour at 360° C. under a pressure of 25 atmospheres. The products consist of 40 grams of gasoline and 81 liters of a gas containing 65.4 liters of hydrogen and 72 grams of acetic acid.

The later discovery that the lower alkyl chlorides can be condensed with carbon monoxide to furnish carboxylic acid chlorides according to the reaction

$$CH_3Cl + CO \longrightarrow CH_3COCl$$

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[60] U. S. Patent 1,519,017, Dec. 9, 1924; assigned to H. A. Gardner.

[61] Schrauth, German Patent 327,048, 1914; *J.S.C.I.*, 1921, 40, 227A.

[62] Bataafsche Petroleum Maatschappij, British Patent 355,866, 1930, *Brit. Chem. Abs.* B, 1932, 56; German Patent 560,907, 1930; *Chem. Abs.*, 1933, 27, 1006; French Patent 690,935, 1930; *Chem. Abs.*, 1931, 25, 1259.

would appear to offer a definite technical method of application of these alkyl chlorides in the synthesis of numerous organic products. According to Frolich and Wiezevich,[63] this reaction proceeds, in the case of methyl chloride, at 700° to 800° C. with an efficiency of over 75 per cent, though the conversion per single passage is limited. A number of catalysts for effecting this combination have been mentioned by Steinhäuser.[64] These include boric acid, phosphoric acid, or an alkali borate or phosphate.

Oxygenated organic compounds are said to result from the action of carbon monoxide on low-molecular weight hydrocarbons, their monochlorides or ethers in the presence of anhydrous aluminum chloride.[64a] From butyl chloride and carbon monoxide a product of the formula $C_6H_{10}O_2$ was obtained.

REACTIONS OF DICHLORINATED PARAFFINS AND CYCLOPARAFFINS

The constitution of the dichloro-compounds produced by the substitutive chlorination of paraffins and cycloparaffins is known only in a relatively few cases. This fact limits the utility of any comprehensive account of the reactions of dichlorinated paraffins and cycloparaffins from the viewpoint of the industrial application of such substances. Only a few of the obviously important reactions of these compounds will therefore be discussed. The 1,2-dichloro-compounds, or olefin dichlorides, are treated in Chapter 20.

Under the influence of light, asymmetric-dichloroethylene ($CH_2:CCl_2$) yielded a completely saturated polymer, the molecular weight of which corresponded to about 50 to 100 original molecules.[64b] When heated to above 120° C. the polymer charred and liberated hydrogen chloride. A mixture of hydrocarbons resulted on heating 1.5 grams of the polymer with 1 gram of red phosphorus and 7 grams of 70 per cent hydriodic acid. Extraction of the hydrocarbon mixture with boiling benzene gave a soluble fraction having a melting point of about 111° C., which corresponded to about $C_{100}H_{202}$, and an insoluble portion melting at 116° to 117° C. and corresponding to $C_{160}H_{322}$. Further purification by distillation with soda-lime and extraction with ether resulted in the resolution of two hydrocarbons melting at 74° to 75° C. ($C_{36}H_{74}$) and 95° C. ($C_{60}H_{122}$), respectively. Reduction of the polydichloroethylene with zinc dust and acetic acid in a stream of hydrogen chloride furnished a polymer $(C_2HCl)_x$. When heated with aniline for 14 days polydichloroethylene yielded an almost completely halogen-free benzene-soluble product $(CH_2.C{=}NC_6H_5)_x$. Sodium methoxide or ethoxide, trimethylamine, pyridine, or quinoline, however, failed to completely eliminate the chlorine from the polymer.

Perhaps the most important property of the dihalogen derivatives is their decomposition with the formation of diolefins and loss of two molecules of hydrogen chloride, according to the scheme:

$$C_nH_{2n}Cl_2 \longrightarrow 2HCl + C_nH_{2n-2}$$

This decomposition can be brought about by the action of alkalies or by purely thermal means. Very frequently the process can be cut short at the intermediate stage, i.e., with the production of a monochlorinated olefin. Thus, ethylene dichloride can be converted into vinyl chloride[65] by passing through a pumice-filled tube at 600° C., while at higher temperatures acetylene becomes the main product.

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[63] *Ind. Eng. Chem.*, 1931, **24**, 13.

[64] German Patent 561,399, 1928; *Chem. Abs.*, 1933, **27**, 1007; U. S. Patent 1,911,589, May 30, 1933; *Chem. Abs.*, 1933, **27**, 3950; British Patent 308,666, 1928; *Brit. Chem. Abs.* **B**, 1930, 808; all patents assigned to I. G. Farbenindustrie A.-G.

[64a] Hopff, German Patent 512,718, 1927; *Chem. Abs.*, 1931, **25**, 1258; Hopff and Dunkel, German Patent 568,129, 1928; *Chem. Abs.*, 1933, **27**, 2691; both patents assigned to I. G. Farbenindustrie A.-G

[64b] Staudinger and Feisst, *Helv. Chim. Acta*, 1930, **13**, 832; *Chem. Abs.*, 1931, **25**, 487.

For the elimination of hydrogen chloride from various chloro-derivatives of hexane and heptane by thermal treatment in the presence of various contact materials, such as unglazed porcelain alone or treated with barium chloride, Faragher and Garner[66] found that the dichloro-compounds were less satisfactory than the monochlorides. There was much more extensive decomposition and greater difficulty in separating all the chlorine from dichloro-compounds. Table 140 shows the yields and iodine values of the products obtained by Faragher and Garner on decomposing a dichlorohexane, d^{20}_{0} 1.067, at various temperatures in the presence of the above catalysts.

TABLE 140.—*Decomposition of Dichlorohexane.*

Catalyst	Temp. ° C.	Yield Per Cent	Condensate	
			d^{20}_{4}	Iodine No.
Unglazed porcelain alone	350	75	0.874	188
	400	95	0.896	160
	450	90	0.875	176
	500	—	0.876	170
Unglazed porcelain + $BaCl_2$	200	88	0.996	64
	300	88	0.942	123
	400	84	0.920	142

(The theoretical iodine number for a hexadiene is 620.)

In the course of their work on the production of drying oils from higher molecular weight petroleum hydrocarbons, Gardner and Bielouss[67] observed that the dissociation point of the polychloro-compounds, derived from these hydrocarbons, lies between 120° C. and 250° C. and that practically complete dechlorination can be effected by heating them to 250° C. without the aid of any other agents. Here again, however, the iodine numbers of the resulting hydrocarbons were always considerably lower than the calculated values, probably on account of cyclicization.

The dichloro- and trichloro-derivatives of cyclohexane were found by Faragher and Garner to be more readily decomposed than the chlorides of the paraffin hydrocarbons. Thermal treatment of a dichlorocyclohexane, of d^{20}_{0} 1.179, gave products of the following iodine numbers (Table 141) when subjected to the action of unglazed porcelain and alumina, respectively, at various temperatures. The theoretical iodine number of the expected dihydrobenzene is 317.

TABLE 141.—*Decomposition of Dichlorocyclohexane.*

Temperature ° C.	Iodine Number of the Products	
	Unglazed Porcelain	Alumina
200	113	132
250	146	167
300	175	170
400	188	117

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[65] Böeseken and Bastet, *Rec. trav. chim.*, 1914, 32, 184; Baxter, Edwards and Winter, British Patent 363,009, 1930; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1932, 331.

[66] *J.A.C.S.*, 1921, 43, 1715.

[67] *Ind. Eng. Chem.*, 1922, 14, 619.

Decomposition of a trichlorocyclohexane (d^{20}_{0} 1.266) at 250° C. in the presence of unglazed porcelain furnished a 10 per cent yield of benzene, determined by conversion into m-dinitrobenzene.

One of the earlier contemplated uses of the above reactions was for the production of certain conjugated diolefins, such as isoprene, capable of being polymerized to rubber-like products. Graul, Hanschke and Webel[68] described the preparation of isoprene and similar diolefins by treatment of dichlorinated derivatives of pentane and hexane with catalysts, such as alumina and barium chloride at elevated temperatures and under reduced pressure.[68a] Schmidt, Hochschwender and Eichler[69] also eliminated hydrogen chloride from mono- and dichlorocyclohexanes by thermal treatment in the presence of catalysts. Chlorination of a fraction of Caucasian petroleum of boiling point 68° to 73° C. is said to yield a dichloro-methylcyclopentane which may be resinified to a glassy solid, almost devoid of color, by heating with zinc chloride in glacial acetic acid.[70]

The chlorine atoms in di- and poly-chlorinated paraffins may be substituted by hydroxyl, alkoxy-, cyano-, acetoxy-, phenoxy-, amino-, and other groups using reactions similar to those employed in the case of the monochlorides. Under some conditions, however, while one chlorine atom is replaced by another group, a second chlorine atom is eliminated in the form of hydrogen chloride so that an unsaturated product is obtained.[71] Bosshard and Strauss[72] have described the conversion of a dichloroparaffin, melting point 40° to 60° C., and obtained by the chlorination of paraffin wax, into a *phenoxychloroparaffin* by heating it with phenol and potassium carbonate.

The manufacture of certain *nitrogenous derivatives of the higher paraffin hydrocarbons* has been described by the I. G. Farbenindustrie A.-G.[73] Halogenated derivatives of paraffins of more than 8 carbon atoms are heated with ammonia in aqueous or alcoholic solution preferably under pressure. Instead of ammonia, substances capable of yielding this compound may be used, such as ammonium carbonate or urea, together with a catalyst, such as copper or a copper compound. Methods have also been proposed[74] for making *sulphonated derivatives of higher paraffin hydrocarbons.* These higher paraffins (above C_8H_{18}) are halogenated to introduce more than two halogen atoms per molecule and the halogenated products are treated with aqueous or alcoholic solutions or suspensions of alkali or alkali carbonates, and finally with a sulphonating agent in the presence or absence of a diluent (carbon tetrachloride) or of compounds which assist the reaction (e.g., fatty acids or their anhydrides or chlorides). Wetting agents have also been prepared by condensing glycol with chlorinated petroleum in the presence of sodium or with piperidine or p-aminophenol in the presence of copper.[74a]

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[68] U. S. Patent 1,298,929, Apr. 1, 1919; assigned to Alien Property Custodian; *Chem. Abs.*, 1919, **13**, 1954; Badische Anilin- und Soda-Fabrik, French Patent 434,586, 1911; *Chem. Abs.*, 1912, **6**, 2313; French Patent 435,312, 1911; *Chem. Abs.*, 1912, **6**, 2548.

[68a] The production of isoprene by these methods is mentioned in Chapter 4 and the polymerization of isoprene to synthetic rubbers, in Chapter 26.

[69] See footnote 21.

[70] British Patent 23,543, 1912; *J.S.C.I.*, 1913, **32**, 876.

[71] The same phenomenon occurs with other di- and poly-halogen products. Thus isobutylene dibromide reacts with sodium acetate to furnish 33% of isobutenyl acetate, $CH_2 = C(CH_3)CH_2OOCCH_3$. Trimethylene dibromide reacts similarly. (Krassoursky and Schenderowitch, *Ukraine Chem. J.*, 1925, **1**, 633; *Brit. Chem. Abs.* **A**, 1926, 1022.)

[72] German Patent 344,878, 1923; assigned to Elektrochemische Werke G.m.b.H.

[73] British Patent 339,962, 1929; *Brit. Chem. Abs.* **B**, 1931, 194.

[74] I. G. Farbenindustrie A.-G., British Patent 344,829, 1929; *Chem. Abs.*, 1932, **26**, 267; British Patent 352,989, 1930; *Brit. Chem. Abs.* **B**, 1931, 1090; French Patent 40,987, 1931; *Chem. Abs.*, 1933, **27**, 1524; addition to French Patent 703,466, 1930; *Chem. Abs.*, 1931, **25**, 4414; see Chapter 46 for more complete details of the production of sulphonated hydrocarbons.

[74a] I. G. Farbenindustrie A.-G., French Patent 709,626, 1931; *Chem. Abs.*, 1932, **26**, 1403.

The products obtained by heating poly-chlorinated paraffin hydrocarbons of more than 8 carbon atoms, with alkalies in aqueous or alcoholic media, best under pressure and in the presence of catalysts, are said to be mainly unsaturated hydrocarbons containing one or more hydroxyl groups. These products are reported to be valuable as greasing and lubricating agents in the leather and textile industries. They may be sulphonated to produce wetting and emulsifying agents.[75]

Curme and Lommen[76] obtained ethylenediamine by treating dichloroethane with a large excess of ammonia. Aliphatic diamines may also be prepared by a similar reaction using one or more oxides or salts of such metals as copper and zinc, capable of forming complexes with the diamine, under heat and pressure.[77] By reacting dichloroethane with an excess of aniline at 115° C. in the presence of a small proportion of water and a large amount of NN′-diphenylethylenediamine, Morton[78] obtained aromatic derivatives of 1,2-diaminoethane, melting at 65° C.

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[75] I. G. Farbenindustrie A.-G., French Patent 699,877, 1930; *Chem. Abs.*, 1931, 25, 3480. *Cf.* French Patent 734,943, 1932; *Chem. Abs.*, 1933, 27, 1116.

[76] U. S. Patent 1,832,534, Nov. 17, 1931; assigned to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1932, 973.

[77] Goodyear Tire and Rubber Co., French Patent 739.317, 1932; *Chem. Abs.*, 1933, 27, 2159; British Patent 393,093, 1932; *Brit. Chem. Abs.* **B**, 1933, 777.

[78] U. S. Patent 1,836,486, Dec. 15, 1931; *Brit. Chem. Abs.* **B**, 1933, 216.

Chapter 35

Extraction of Nitrogen Compounds from Petroleum

In coal oil and shale oil there are present aromatic compounds of nitrogen which can be identified with comparative ease. Their analytical constants of identification have long been established. This, however, is far from being true in the case of the nitrogen compounds of petroleum for here are presented an astonishing variety of nitrogen bodies of unknown structure many of which, according to present indications, fall into the class of hydroaromatics.

The study of this array of hydroaromatic bases opens to chemists a new domain of great scientific interest and possible practical value. For hydroaromatic bases are closely allied to the alkaloids. To change hydroaromatic bases to alkaloids it is only necessary to make a proper placement of oxygen in the molecule.

Further, indications point to the presence in petroleum of bases containing naphthene rings of 5 carbon atoms, particularly polycyclic compounds composed of naphthene and aromatic or hydroaromatic nuclei. Following a common practice in referring to naphthenic acids these naphthene compounds of nitrogen may be designated naphthenic bases. In due course there may be expected an appropriate correlation between naphthenic bases and their corresponding hydrocarbon relatives.

The nitrogen content of petroleum oils is rather low; in most instances being about 0.1 per cent or less.[1] The two extremes however seem to be represented by American oils. The Pennsylvania oils have the lowest nitrogen content, 0.008 per cent having been reported,[2] and the California oils [3] contain the highest percentage of nitrogen. Japanese and South American oils also appear to have a nitrogen content considerably higher than the average. Paraffin base oils, like those from Pennsylvania, which show such a small nitrogen content, can probably be considered as practically nitrogen-free or as containing only a trace of nitrogen, as such nitrogen determinations are well within the experimental error of the analysis. Poth, Armstrong, Cogbrun and Bailey [4] in their investigation of the nitrogen content of a large number of California crude oils found the maximum quantity to be about 0.82 per cent. On the assumption that the average molecular weight of the nitrogen compounds was represented by the formula $C_{10}H_{13}N$, which was admitted to be probably low, Mabery has suggested that the percentage of nitrogen in an oil should be multiplied by 10 to give the percentage of nitrogen compounds.

By distillation *in vacuo* of nitrogen bases extracted with sulphuric acid from California petroleum, Mabery [5] obtained several fractions, which corresponded in analyses and molecular weights with the following: [6]

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[1] Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, 1932, 170.

[2] Beilby, *J.S.C.I.*, 1891, **10**, 120.

[3] Mabery, *J.S.C.I.*, 1900, **19**, 502, reported 2.39% nitrogen in some California oils.

[4] *Ind. Eng. Chem.*, 1928, **20**, 83.

[5] *Loc. cit.*

[6] There appeared to be some doubt as to the number of hydrogen atoms in the molecule. Mabery and Wesson (*J.A.C.S.*, 1920, **42**, 1015) stated that the final main fractions, obtained by distillation at 50 to 90 mm. pressure, were as here given.

B.P. °C.	Formula	B.P. °C.	Formula
130–140	$C_{12}H_{17}N$	223–225	$C_{15}H_{19}N$
197–199	$C_{13}H_{15}N$	243–245	$C_{16}H_{19}N$
215–217	$C_{14}H_{19}N$	270–275	$C_{17}H_{21}N$

The bases dissolved in acids to form salts which could be easily decomposed. Crystalline precipitates could be formed with platinum chloride though the platinum content was about 2 per cent lower than the calculated value. Neither the picrates nor oxalates were well-defined salts. The only product which could be identified from oxidation with chromic acid was a small quantity of acetic acid, which was obtained from the bases containing methyl side chains. With potassium permanganate in neutral or alkaline solution a part of the nitrogen was evolved as ammonia, while in acid solutions all of the nitrogen was evolved as nitrogen. The bases formed quaternary salts when heated with ethyl iodide. While no definite structures could be given for any of the bases, the evidence seemed to indicate the existence of a tetrahydroquinoline ring as a part of the molecule, and also a benzene ring.

Later Mabery and Wesson[7] oxidized some of these fractions with neutral potassium permanganate and obtained oxidation products which could be separated into alcohol-soluble and alcohol-insoluble portions. The alcohol-insoluble portions were dissolved in hot water, from which insoluble silver salts were obtained. Their analyses led Mabery and Wesson to believe them to be the tetra-silver salts of pyridine pentacarboxylic acid.[8] This conclusion appeared to be confirmed when the corresponding barium salt on dry-distillation yielded a distillate whose principal component was pyridine. From the soluble portions of the oxidation products, silver salts were separated, the analyses of which indicated them to be di-silver salts of methylpyridine tetracarboxylic acid.

Oxidation of the fractions with permanganate failed to yield appreciable quantities of aliphatic acids; the small quantities which were formed possessed the properties of the lowest molecular weight acids, acetic and propionic. These facts would tend to argue against the presence of any side chains of considerable length in the molecule.

Oxidation with chromic acid followed by the dry distillation of the calcium salt yielded a product which, from the melting point of its picrate,[9] was probably β-methylquinoline. On the assumption that the compound formed during the distillation of the calcium salt was β-methylquinoline then this would indicate the formation of β-methylcarboxyquinoline (by oxidation) as this substance is known to be resistant to oxidation, in certain instances, before disruption of the quinoline molecule takes place.

On treating the bases with reducing agents, such as tin and hydrochloric acid, zinc and acetic acid, sodium amalgam and alcohol, not only was the nucleus hydrogenated, but the nitrogen was reduced from the tertiary to the secondary state. The latter condition was indicated by the formation of a nitroso-amine when the reduced base was treated with nitrous acid.

When dissolved in organic solvents and treated with either bromine or iodine the original bases apparently formed addition compounds, as well as substitution products. These same bases also reacted with phthalic anhydride in the presence of anhydrous zinc chloride to form phthalones, while fuming sulphuric acid converted them to sulphonated compounds. Platinic chloride reacted with the bases to form chloroplatinates, though on attempting to recrystallize these salts from hot water, decomposition was noted. Attempts to break the nitrogen ring, using von Braun's method,[9a] that is, benzoylation of the base followed by treatment with phosphorus pentachloride, yielded negative results.

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[7] *J.A.C.S.*, 1920, 42, 1014; *Chem. Abs.*, 1920, 14, 1831.

[8] On attempting to prepare the free pyridine carboxylic acids from their salts Mabery and Wesson reported (*J.A.C.S.*, 1920, 42, 1021) that "only semi-liquid or amorphous products were obtained, however, in place of the acids." Hantzsch (*Ann.*, 1882, 215, 62) reported that after evaporation of a concentrated solution of pyridine pentacarboxylic acid to a syrupy consistency on a water bath the liquid slowly solidifies to a mass of microscopic crystals on cooling. He also emphasized the difficulty of obtaining salts of this acid free of potassium. Weber (*Ann.*, 1887, 241, 15-16) stated that by the decomposition of the silver salt, free of potassium, with hydrogen sulphide he was able to obtain pyridine pentacarboxylic acid with 3 molecules of water from an aqueous solution. It is possible therefore that Mabery and Wesson were not working with the pure acids.

[9] No other method for the identification of this product was reported.

From the results of their work Mabery and Wesson drew the following conclusions. (1) These bases consist principally of alkylated quinolines or isoquinolines.[10] (2) Three alkyl groups are united to the α, β, and γ-carbon atoms of the nitrogen ring. In the lowest member of the series, $C_{12}H_{13}N$, these three side chains must be methyl groups since the quinoline radical accounts for 9 carbon atoms. (3) Phthalone formation[11] requires a $—CH_2$ or $—CH_3$ group in the α- or γ-position in the nitrogen ring. (4) The non-formation of high molecular weight aliphatic acids as oxidation products indicated that none of the side-chains were over 4 carbon atoms in length. (5) The other reactions, such as those with halogens, with reducing agents, with fuming sulphuric acid, etc., also conform with these conclusions.

It is also pointed out by Mabery and Wesson that "all of the fractions of the series of bases represent mixtures which can be fairly well separated into stages as regards molecular weights, but are difficult to separate into individual substances. The facts cited in experimental evidence for the character of the compounds represents what might be expected from a mixture of quinoline and possibly isoquinoline derivatives, a small part more, a small part less highly alkylated than the average, and containing perhaps a small percentage of hydrogenated nuclei or of pyridine derivatives."

Bailey,[12] however, points out that very little or practically none of the nitrogen compounds in crude oils can be extracted with dilute acid, indicating that such compounds are of a non-basic character. The distillates from such crude oils, however, contain nitrogen compounds which are basic, together with compounds which are inert toward acids. These basic compounds no doubt result from the decomposition of more complex substances during distillation, and generally the higher the temperature of distillation the greater the nitrogen content of the distillate.

The complexity of these nitrogen compounds is also shown by the fact that exhaustive fractionation of kerosene (California) bases boiling from 180° to 335° C. failed to yield any component in a pure form. Furthermore, that a number of basic compounds was present in each fraction was indicated by the fact that picrates which separate in a crystalline form were not obtained (except from one fraction boiling around 276° C.). However by extracting with a buffered acid solution, and then fractionally precipitating by the addition of sodium hydroxide, it was possible to concentrate several products which yielded crystalline salts, and were apparently in a pure form.

That the failure to isolate pure substances by fractional distillation was not due to the formation of constant boiling mixtures is indicated by the following consideration. So far fractional distillation has yielded a mixture of products which, at atmospheric pressure, boil within a range of a few degrees. Also the fractional distillations have been carried out at low pressures, to avoid decomposition of the nitrogen bases, and it is not improbable that with the use of a reflux column it is possible to separate bases in the fractions with components boiling within a range of two degrees. In fact from one fraction of bases two compounds having the formula $C_{12}H_{18}N$ and boiling at 280.6° C. and 278.9° C. (both at 746 mm.), respectively, and also the substance $C_{16}H_{25}N$ boiling at 278.2° C., have been obtained in pure conditions. The residual bases, after the removal of these three compounds, boiled at a constant temperature.

[9a] *Ber.*, 1904, **37**, 2818.

[10] *Cf.*, Mabery's earlier views concerning the structure of these bases (*J.S.C.I.*, 1900, **19**, 505).

[11] Bailey (private communication) has reported that the hydroaromatic base, $C_{16}H_{25}N$, obtained from a petroleum distillate condenses with phthalic anhydride exactly as quinaldine does. As this base is not a quinoline derivative, phthalone formation apparently, therefore, cannot be taken as indication of the structure of the molecule.

[12] Poth, Armstrong, Cogburn and Bailey, *Ind. Eng. Chem.*, 1928, **20**, 83; Poth, Schulze, King, Thompson, Slagle, Floyd and Bailey, *J.A.C.S.*, 1930, **52**, 1240.

While these basic nitrogen compounds are extracted by the sulphuric acid used in refining,[13] the isolation of such compounds from the acid extract would prove expensive and seriously interfere with plant routine. There is also the possibility of sulphonation, oxidation or polymerization of the nitrogen compounds by the acid. Bailey and his co-workers therefore used the sulphur dioxide extract obtained by the Union Oil Company of California in the refining of kerosene distillates by the Edeleanu process. Sulphur dioxide acts merely as a solvent, and, after its recovery, the residue contains the nitrogen bases mixed with a large quantity of hydrocarbon oil. From this residue the nitrogen bases were extracted with dilute sulphuric acid and the water-insoluble bases obtained by the addition of sodium hydroxide.[14] In this manner 50 liters of water-insoluble bases were obtained from 150 barrels of residue. These bases contained a small amount of hydrocarbon oil and from 0.3 to 0.6 per cent of sulphur.

A number of the individual nitrogen bases have been isolated and several identified. The preparation and properties of the latter will be described briefly.

The first of the nitrogen compounds to be identified was 2,3,8-trimethylquinoline,[15] which comprises about 18 per cent of the fraction boiling at 276° to 277° C., at atmospheric pressure. The other compounds which have been isolated from this same fraction are the isomeric compound $C_{12}H_{18}N$, and the base having the formula $C_{16}H_{25}N$. The separation of 2,3- as well as 2,4-dimethylquinoline from the fraction boiling around 265° C. has also been announced. These are well-known synthetic products which had not been obtained previously from a natural source.

One method of isolating the 2,3,8-trimethylquinoline was by dissolving the fraction in 50 per cent acetic acid and then precipitating it as the picrate. Mixed with this is the picrate of the substance $C_{16}H_{25}N$; in contrast to the former, it is readily soluble in both benzene and alcohol, and separation of these two picrates was therefore easily effected. Another method of isolation was by means of its acid sulphate. This was obtained by treating the particular fraction with 50 per cent sulphuric acid. Associated with this sulphate is a small quantity of the sulphate of another base, $C_{12}H_{18}N$. This latter compound, not yet identified, is an odorless solid, melting at 43° C. and boiling at 278.9° C. (748 mm.).

To prepare the free base either the picrate or the sulphate is heated with ammonium hydroxide, and the base separates as an oil. The base is then dissolved in ether, the solution washed and the ether allowed to evaporate. Recrystallization from 50 per cent alcohol yields crystals melting at 55° to 56° C. and boiling with partial decomposition at 280° C. (at 747 mm.).

Proof of the structure of this new base was confirmed through its synthesis, from tiglic aldehyde and o-toluidine in the presence of hydrochloric acid.[16] Derivatives of the synthetic product, such as the sulphate, hydrochloride, nitrate, and picrate, as well as a number of its metallic salts such as those with platinum and gold chlorides, were found to be identical with those prepared from the kerosene base.

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[13] Campbell (U. S. Patent 1,907,318, May 2, 1933; *Chem. Abs.*, 1933, 27, 3601), for example, decolorized hydrocarbons by extraction of the bases with sulphuric acid.

[14] See also, Ihrig, U. S. Patent 1,671,721, May 29, 1928; assigned to S. E. Campbell and to Associated Oil Co.

[15] King and Bailey, *J.A.C.S.*, 1930, 52, 1245.

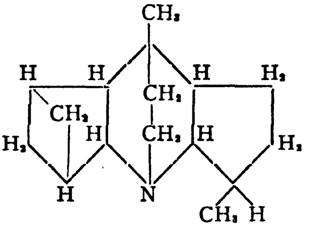
[16] *Cf.* Rohde, *Ber.*, 1887, 20, 1911.

Other reactions also confirmed the structure of the base. Its failure to react with methyl iodide to form the quarternary ammonium salt indicated steric hindrance due to substituents in the 2 and 8 positions. The presence of methyl groups at the 2 and 3 positions was indicated by the fact that the base condensed with two and not three molecules of formaldehyde. Oxidation of this base with chromic acid, followed by distillation over soda-lime yielded the well-known 2,3-dimethylquinoline. This was further evidence of the presence of methyl groups in the 2 and 3 positions. Similarly oxidation of the formaldehyde derivative yielded a dimethylquinolinic acid, which in turn on distillation from soda-lime yielded 3,8-dimethylquinoline. The synthesis of this new quinoline, by Bailey and King, from o-toluidine, propinoic aldehyde and methylal is further proof of its structure.

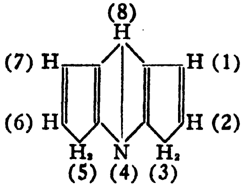
It is of interest to note that an examination of the different distillation fractions failed to reveal any case of optical activity.

The hydroaromatic base of the formula $C_{16}H_{25}N$ is of unusual interest because it represents a new type of nitrogen compound of the cyclopentane type and is probably the forerunner of structurally similar bases occurring in petroleum distillates. The base $C_{16}H_{25}N$ is obtained from the picrate by decomposing with ammonium hydroxide,[17] washing well with water, and drying in a current of air at 100° C. As a final purification the product can be distilled at low pressures (10 to 15 mm.). The substance is a colorless, odorless, optically inactive oil, which is only very slightly soluble in water but soluble in the usual organic solvents. It boils at 278.2° C. at 746 mm. pressure, and has the following physical constants: d_4^{20} 0.9391 and n_D^{20} 1.5129.

The structure assigned to this compound[18] is



This compound is therefore a derivative of the substance,



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[17] Thompson and Bailey, *J.A.C.S.*, 1931, 53, 1002.

[18] This formula, and also formulas (1) and (II) for products obtained by the action of nitric acid on this base, give a better interpretation than the ones formerly assigned (*J.A.C.S.*, 1931, 53, 1002) because of the fact that the $C_{16}H_{25}N$ base behaves as a completely saturated molecule. Private communication from Dr. Bailey. See also Armendt and Bailey, *J.A.C.S.*, 1933, 55, 4145.

for which the name pyrindacine has been adopted. The systematic naming of the compound $C_{16}H_{25}N$ would therefore be decahydro-3,8-dimethyl-5,7-methano-4,8-ethanopyrindacine. In view of the large number of bases which occur in petroleum distillates it is possible that the product $C_{16}H_{25}N$ is one of a series of naphthene compounds of nitrogen, or naphthenic bases.

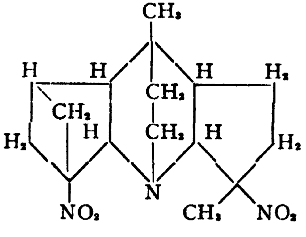
This compound $C_{16}H_{25}N$, is unusually stable toward permanganate in both neutral and alkaline solutions, and also toward oxidation with chromic acid in sulphuric acid solution. It is, however, quite readily attacked by permanganate in an acid solution. It can also be oxidized by fuming sulphuric acid with the evolution of sulphur dioxide when the mixture is heated just above 200° C. Its reaction with hot nitric acid (specific gravity 1.260) yielded several products which were of aid in establishing its structure, and which are discussed a little later.

As it is a basic compound it forms the usual salts such as the hydrochloride, nitrate, acid sulphate and picrate, as well as metallic salts such as those with platinic chloride, mercuric chloride and zinc chloride. Heated with methyl iodide it yields quantitatively the methiodide derivative. Results thus far obtained indicate that it can be neither hydrogenated nor dehydrogenated.

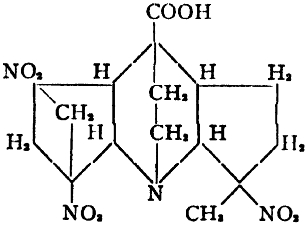
Both the naphthenic base ($C_{16}H_{25}N$) and 2,3,8-trimethylquinoline form loose addition products with bromine, though their behavior is slightly different. The *naphthenic base,* when dissolved in chloroform, excess bromine added, and the chloroform evaporated, yields a red, oily residue. The addition of picric acid to an alcohol solution of the residue yields the picrate of the original base. When treated with bromine water the naphthenic base forms a viscous, red-brown gum soluble in glacial acetic acid, and which is converted to the original base by sodium hydroxide solution. Both of these reactions indicate a loose combination of the bromine with the base. The *2,3,8-trimethylquinoline,* when dissolved in chloroform and bromine added, immediately yields a light yellow needle-like product. This crystalline product is converted to the original compound when treated with a solution of sodium hydroxide.

An unusual property of a saturated hydrocarbon is the nitration of methylcyclopentane with the formation of a mono-nitro derivative. Here the reactive hydrogen is joined to the tertiary carbon in the five-membered ring. Under similar conditions the $C_{16}H_{25}N$ base yields a dinitro compound, $C_{16}H_{23}(NO_2)_2N$, which suggests that two cyclopentane complexes are involved in this reaction. (See formula I.)

(I)

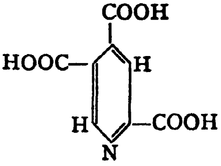


(II)



A second product of the action of nitric acid on the naphthenic base has the composition $C_{16}H_{20}O_8N_4$. Titration showed this substance to be a mono-basic acid, due to the oxidation of the methyl in position 8 to a carboxyl, and three nitro groups entering the molecule are tentatively assigned to positions 3, 5, and 7, respectively.

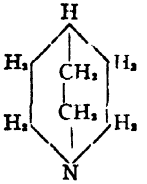
Another product of the nitric acid reaction is berberonic acid, identified by comparison with berberonic acid prepared by oxidation of the alkaloid berberine with nitric acid.[18a] The formation of this acid under similar conditions from



berberonic acid

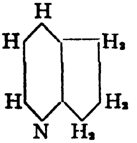
an alkaloid and from the hydroaromatic base[4] must be accepted as a proof that the nitrogen in both compounds is present in a six-membered ring.

There are certain interesting structural relationships between the pyrindacine base and other natural products. One of its ring nuclei is quinuclidine,



and the same complex has been established as present in the alkaloids, quinine and cinchonine.

The cyclopentane ring with a methylene bridging as pictured in the formula of the naphthenic base brings out a structural analogy in this part of the molecule with the newly discovered bi-cyclic naphthenic acids.[19] The isolation of the aromatic base, 5,6-dihydropyrindine



from shale oil,[20] along with its subsequent synthesis,[21] strengthens the claim of the pyrindacine structure of the $C_{16}H_{25}N$ base.

Later, Perrin and Bailey [22] developed a method for the separation of aromatic from non-aromatic bases which they term "cumulative extraction". The resolution is dependent on the solubility of the hydrochlorides of non-aromatic bases as compared with a lesser solubility of aromatic base hydrochlorides in chloroform or ethylene dichloride. Accordingly the bases are dissolved in an excess of 1 :1 hydrochloric acid and the solution is extracted with the organic solvent. The aqueous layer, which contains a high concentration of aromatic base hydrochlorides, is extracted several times with chloroform, and the chloroform layer with water. The process is controlled by refractive index determinations. For the separation of aromatics from small amounts of non-aromatics the bases may be converted in acetone solution to sulphates. The aromatic sulphates separate from this solvent in crystalline form.

[18a] *Cf.* Mayer, *Monatsh.*, 1892, **13**, 344; *Ber.*, 1892, **25**, Ref. 582; *Chem. Soc. Abs.*, 1892, **62**, 1357.

[19] Von Braun, Deuser, Heymons, Mannes, May, Reuter, Anton, Keller, Friehmelt, Schörning, *Ann.*, 1931, **490**, 100; *Brit. Chem. Abs.* **A**, 1931, 1396; *Chem. Abs.*, 1932, **26**, 2306; von Braun, *Z. angew. Chem.*, 1931, **44**, 661; *Chem. Abs.*, 1932, **26**, 584; *Nat. Pet. News*, 1932, **24** (8), 28; *Chem. Abs.*, 1932, **26**, 4702.

[20] Eguchi, *Bull. Chem. Soc. Japan*, 1928, **3**, 239; *Chem. Zentr.*, 1929, **100**, 331.

[21] Thompson and Bailey, *J.A.C.S.*, 1931, **52**, 1002.

[22] *J.A.C.S.*, 1933, **55**, 4136.

By employing the method of cumulative extraction, Perrin and Bailey[22] isolated 2,4,8-trimethylquinoline, and Lake and Bailey,[23] 2,8-dimethylquinoline from the kerosene bases. 2,4,8-Trimethylquinoline was obtained from an extraction of a fraction of the bases of boiling point 273° C. Its hydrochloride is readily soluble in water and the sulphate in acetone; it was separated from the accompanying 2,3,8-trimethylquinoline by use of these solvents. The picrate, which crystallized from alcohol in slender rectangular plates with melting point 193° C. was isolated. The phthalone of 2,4,8-trimethylquinoline was formed by heating the base with phthalic anhydride for three hours at 200° C., dissolving the melt in concentrated sulphuric acid and pouring it onto crushed ice. The phthalone crystallized from alcohol in yellow microscopic needles melting at 282° C.

The isolation of 2,8-dimethylquinoline was accomplished by cumulative extraction of a 253° to 256° C. fraction of kerosene bases. From 6420 cc. of bases, 285 cc. of aqueous solution was obtained, which represented 4.6 per cent of the initial material. This was evaporated to a small volume and chilled. The smeary mixture was washed with a small amount of cold acetone and the residue recrystallized from alcohol. The yield of practically pure hydrochloride was 32 grams (0.4 per cent). Derivatives prepared were the acid sulphate, perchlorate, mercuric chloride salt and phthalone.

Biggs and Bailey,[24] continuing the investigation, isolated 2,4- and 2,3-dimethylquinoline by extraction with sulphur dioxide. Sulphur dioxide forms addition compounds with both aromatic and non-aromatic bases; some of these compounds are fairly stable whereas others dissociate rapidly at room temperature. A partial separation of the bases was accomplished by taking advantage of this difference in reactivity. After a sulphur dioxide separation of a fraction of kerosene bases of boiling point 263° to 267° C., one portion of the bases was treated with an alcoholic solution of picric acid. The precipitant was washed with alcohol, and leached with hot glacial acetic acid. 2,4-Dimethylquinoline picrate separated in long orange-colored needles and was then recrystallized from 95 per cent alcohol. A product melting at 194° C. was obtained. It was found to be identical with 2,4-dimethylquinoline, synthesized according to a method by Fischer.[25]

The picrates difficultly soluble in glacial acetic acid were recrystallized from that solvent. Microscopic hexagonal prisms melting at 231° C. were formed. This base, liberated from the picrate, proved identical with 2,3-dimethylquinoline synthesized by a method of Eliasberg and Friedländer.[26] It is a white crystalline solid melting at 67° C. and boiling at 273° C. (750 mm.).

Armendt and Bailey[27] investigated the fraction of kerosene bases within the boiling point range 215° to 216° C. They isolated a base $C_{13}H_{21}N$ by fractional crystallization of picrates. The base was a colorless oil, with not unpleasant odor, insoluble in water and miscible in all proportions with common organic solvents. Its melting point was 24.5° C.; boiling point, 225.6° C. at 750 mm. The mercuric chloride, the chloroplatinate, acid-sulphate, and picrate were prepared. The base was not identified, however. Its reactions and behavior were compared with the base $C_{16}H_{25}N$, previously mentioned, described by Thompson and Bailey.[28] Neither of these bases could be hydrogenated or dehydrogenated and prolonged heating with alkaline permanganate had no oxidizing effect. Although the $C_{16}H_{25}N$ compound reacted with methyl iodide, the methiodide of $C_{13}H_{21}N$ was not formed under similar conditions. The following formula was selected provisionally for the compound $C_{18}H_{21}N$:

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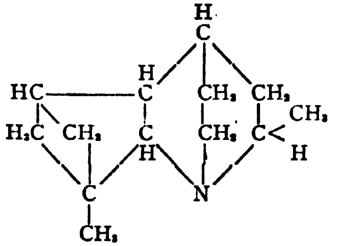
[23] *J.A.C.S.*, 1933, 55, 4143.
[24] *J.A.C.S.*, 1933, 55, 4141.
[25] *Ber.*, 1886, 19, 1037.
[26] *Ber.*, 1892, 25, 1754.
[27] *J.A.C.S.*, 1933, 55, 4145.
[28] *Loc. cit.*



It is certain that petroleum distillates, and this applies especially to California petroleum, contain a host of hydroaromatic bases. Bailey is of the opinion that many of them are of the pyrindine or pyrindacine type and that they will be found to differ from one another in the state of saturation, in the position of double bonds, in the number and position of side-chains and in the nature of bridging in the ring nuclei. In any event, it is highly probable that the importance of the cyclopentane complex, i.e., naphthenic structure, will be brought into greater prominence as the true nature of the petroleum hydroaromatic bases is revealed.

Just why *hydroaromatic* bases should come from petroleum and be absent in coal, shale and bone distillates is a puzzle for which no explanation so far has been offered. Furthermore, it is of interest to note that none of the *aromatic* bases, so far encountered in the investigation of kerosene bases by Bailey and his co-workers, has been obtained previously from any other natural source.

In spite of the satisfactory interpretation of the reactions of the base $C_{16}H_{25}N$ by means of the structure assigned, there are still several other trinuclear cyclic arrangements possible. In the absence of the synthesis of this base absolute proof of the structure presents a very difficult problem in orientation.

Nitrogen compounds belonging to the pyridine series have been isolated by Eguchi[29] from one fraction obtained on the distillation of Fushun (Japanese) shale tar. No primary or secondary bases were found and only traces of pyrroles.

The crude shale tar was separated into the following fractions: 3 per cent boiling up to 200° C.; 25 per cent from 200° C. to 250° C.; 27 per cent from 250° C. to 300° C.; 23 per cent from 300° C. to 350° C.; and 22 per cent residue. On extraction with 30 per cent sulphuric acid 106 liters of the fraction boiling from 220° C. to 250° C. yielded 3550 cc. of bases. Of these bases a fraction of 1965 grams, boiling up to 200° C., was further separated into 56 fractions, and the nitrogen bases separated from the various fractions by means of the addition compounds formed with mercuric chloride. Identification was obtained by oxidizing the compounds to their corresponding carboxylic acids, and also by comparison of their physical properties with those of synthetic materials. The fraction boiling from 128° to 130° C. yielded 2-methylpyridine; that boiling from 143° to 144° C. gave 2,6-dimethylpyridine; the one boiling from 158° to 160° C. yielded both 2,4-dimethyl- and 2,6-methylethyl pyridine; while 2,4,6-trimethylpyridine was obtained from the fraction boiling between 170° and 172° C.

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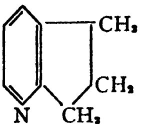
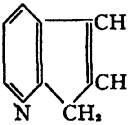
[29] *Bull. Chem. Soc. (Japan)*, 1927, 2, 176; *Chem. Abs.*, 1927, 21, 3196; *Brit. Chem. Abs.* **B**, 1927, 696.

Later Eguchi[30] devised a method for the separation of various methyl pyridines based on the carefully controlled fractional precipitation with picric acid and the purification of the various picrate fractions. Applying this method to the various low-boiling fractions of nitrogen bases from the Fushun shale tar he was able to obtain a series of pyridine derivatives particularly rich in α- and γ-alkyl derivatives. The majority of these were methyl derivatives, though from the last fraction boiling at 200° to 202° C. a new base called pyrindane



was obtained. Bailey,[31] however, has suggested the name pyrindine for the compound



and according to his system of nomenclature pyrindane would become 5,6-dihydropyrindine (*cf.* pyrindacine). The synthesis of 5,6-dihydropyrindine, using cyclopentanone as the initial material, was accomplished later by Thompson[32] and further confirmation of the structure, as suggested by Eguchi, was thus obtained.

Likhushin[32a] removed as much as 0.26 per cent of nitrogen compounds from oil and acid separated from acid sludge. The nitrogen compound separated from the sulphuric acid had the composition: 51.33 per cent carbon, 6.42 per cent hydrogen, 2.49 per cent nitrogen and 41.87 per cent sulphuric acid. Another oil, yellow in color and with a pyridine-like odor, which was separated by steam distillation of the neutralized acid, contained 81.95 per cent carbon, 10.12 per cent hydrogen and 8.40 per cent nitrogen. This latter oil was believed to consist of a mixture of pyridine and quinoline compounds.

The extraction of nitrogen bases from other petroleum distillates and their industrial application has also been suggested. For example, the crude gasoline obtained from the first distillation of petroleum oil is extracted with 25 per cent sulphuric acid, and after separation of the acid and distillate the former is made alkaline and distilled. The nitrogen bases thus obtained after distillation can be used as one of the components of insecticides.[33] The same use can be made also of such bases obtained from the sulphur dioxide extract obtained in the refining of heavier distillates,[34] such as kerosene. The bases obtained from California gas oil by acid extraction followed by steam distillation of the extract are further purified by redistillation or treatment with oxidizing agents. Lubricating oils are said to be improved by the addition of 1 per cent of such bases.[35] As they are added in such small quantity their effect is possibly that of an antioxidant, or inhibitor; as a large group of nitrogen compounds, particularly the organic base type, are known to inhibit the autoxidation of lubricating oil. (See Chapter 40.)

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[30] *Bull. Chem. Soc. (Japan)*, 1928, 3, 227; *Chem. Abs.*, 1929, 23, 391; *Brit. Chem. Abs.* B, 1929, 6.

[31] *J.A.C.S.*, 1931, 53, 1004.

[32] *J.A.C.S.*, 1931, 53, 3160.

[32a] Repts. of the Sci.-Tech. Council of the Petroleum Industry, Session of the Refinery Sect. in Baku in 1929; *Chem. Abs.*, 1931, 25, 5755.

[33] Ihrig, U. S. Patent 1,686,136, Oct. 2, 1928; assigned to S. E. Campbell and Associated Oil Co.; *Chem. Abs.*, 1928, 22, 4789.

[34] Associated Oil Co., British Patent 287,371, 1927; *Brit. Chem. Abs.* B, 1928, 382.

[35] Ihrig, U. S. Patent 1,768,910, July 1, 1930; *Brit. Chem. Abs.* B, 1931, 332.

Orelup [35a] observed that nitrogen bases from oil shale residues can be used to stabilize cracked petroleum distillates.

Still another use for these nitrogen bases is as inhibitors in pickling solutions. Voorhees [36] has prepared a pickling acid from the sludge obtained in the treating of light distillates such as cracked gasoline or kerosene. The sludge is diluted with water to a concentration of about 35 to 40 per cent sulphuric acid; the acid is then removed from the tarry material which separates and is deodorized by steaming. Afterwards this acid can be diluted to the proper concentration for pickling, usually about 6 per cent, and used alone or it can be mixed with pure acid and the mixture used as a pickling solution. As basic nitrogen compounds, such as quinolines, isoquinolines and acridines, are known to be inhibitors in the pickling process there is little doubt that some basic nitrogen compounds remain in the acid obtained from sludge and these are the active inhibitors. Later, Voorhees [37] described the recovery of such bases from cracked petroleum oils and their use in baths for pickling metals.

[35a] U. S. Patent 1,909,069, May 16, 1933; assigned to Patent Fuels and Color Corp.; *Chem. Abs.*, 1933, 27, 3810.

[36] U. S. Patent 1,793,146, Feb. 17, 1931; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1931, 931.

[37] U. S. Patent 1,838,338, Dec. 29, 1931; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1932, 943.

Chapter 36

Oxidation of Petroleum Hydrocarbons. General Considerations. Use of Air, Oxygen or Ozone

The wide variety of oxidation products of petroleum hydrocarbons and their production is a problem of great economic importance. As an illustration of the possibilities in this field, Egloff and Schaad[1] calculated from the amounts of the various paraffin hydrocarbons in commercial fuel gases that 2×10^{12} cubic feet per year of methane, ethane, propane and butane are available for conversion into oxidation products. The alcohols that could be made from such a quantity of gases would total billions of gallons. In addition to alcohols, other substances such as aldehydes or acids, could be made also by oxidation. As previously pointed out, alcohols are being made from the unsaturated gaseous hydrocarbons obtained in cracking operations.[2] These unsaturated hydrocarbons are absorbed in sulphuric acid to form the acid esters which, by hydrolysis, yield alcohols.

The oxidation of petroleum wax to produce high molecular weight acids has received a considerable measure of research and commercial attention. These acids may be converted to fats by esterification with glycerol or glycol. They may be used also in the manufacture of candles and soaps. Furthermore, if the oxidation of wax is not carried completely to the acid stage, intermediate products resembling true waxes are obtained. Such compounds present marked industrial possibilities.

Acids have been made by the oxidation of high-boiling distillates. Such acids appear to be mixtures derived not only from straight-chain or paraffinic but from cyclic hydrocarbons as well. Other products which have been made by the vapor phase oxidation of some of the petroleum fractions are various solvents and oxidized kerosene. For instance, a liquid having a high solvent power for naphthalene has been so prepared.[3] Hydroxy-acids and unsaponifiable oxidized oils have been prepared by liquid and vapor phase oxidation. The utilization of the hydroxy-acids as starting materials for the manufacture of cheap varnish gums or paint film substitutes and of the unsaponifiable oxidized oils for lubricating greases has been suggested.[4]

Artificial asphalts are made by the blowing of heavy pitch-like residues obtained on the distillation of certain crude petroleum oils with air or other oxidizing gases.[5] The changes which take place during such an operation are obviously too complex to be well understood. Hausman[6] states that it is essential to have raw materials containing hydrocarbons which, after cracking and polymerization, help in the formation of asphalts. He is of the opinion that even crude oils containing paraffin wax can be used for the production of asphalt.[7] The lower boiling hydrocarbons present in blown asphalts can be removed by distillation, particularly with steam or under reduced pressure.[8] The subject of asphalt manufacture, however, is one of almost unlimited extent and no attempt to review it will be made here.[9]

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[1] *Oil and Gas J.*, 1929, **27** (43), 156; *Chem. Abs.*, 1929, **23**, 3337.

[2] See Chapters 13, 14, and 16.

[3] von Piotrowski and Winkler, *Brennstoff-Chem.*, 1933, **14**, 208; *Brit. Chem. Abs.* **B**, 1933, 611.

[4] James, *Chem. Met. Eng.*, 1921, **25**, 1128; *ibid.*, 1922, **26**, 209; Furness, *J.S.C.I.*, 1923, **42**, 199; *ibid.*, 1923, **42**, 358.

[5] See Hausman, *Nat. Petr. News*, 1932, **24** (36), 26; Sakhanov and Logvinova, *Gross. Neft.*, 1931, **1** (6-7), 69; *Chem. Abs.*, 1932, **26**, 4943; Egloff and Levinson, *J. Inst. Pet. Tech.*, 1933, **19**, 504; Abson, *Oil and Gas J.*, 1933, **31** (45), 69; *Chem. Abs.*, 1933, **27**, 3597; Mizusima and Yamada, Japanese Patent 93,247, 1931; *Chem. Abs.*, 1933, **27**, 1503.

[6] *Petroleum Z.*, 1932. **28** (8) 1; *Brit. Chem. Abs.* **B**, 1933, 418.

GENERAL CONSIDERATIONS

Petroleum hydrocarbons can be oxidized in either the liquid or vapor phase, the determining factor in a large measure being the type of hydrocarbon which is being treated. For hydrocarbons which are normally gases or low boiling liquids, vapor phase oxidation is almost universally used. For paraffin wax and heavy oils, liquid phase oxidation is used to better advantage. The temperatures employed vary from about 120° to 150° C. for liquid phase oxidation, to cover 500° C. for some vapor phase oxidation processes. Similarly, the pressures used cover a wide range.

The most generally used oxidizing agent is air, though pure oxygen or ozone is sometimes substituted for it. The oxides of nitrogen, particularly the dioxide, either alone or mixed with air or oxygen, are also employed occasionally. In some processes these oxides appear to act only as catalysts, though in others they serve as actual oxidizing agents.

When oxygen or air is used as the oxidizing agent the products include alcohols, aldehydes, ketones, and acids. Further oxidation eliminates the carboxyl group, yielding carbon dioxide and a molecule containing one less carbon atom. With unsaturated hydrocarbons oxidation is often accompanied by a rupture of the molecule at the double bond.

Two general theories have been offered for the mechanism of oxidation: the hydroxylation and the peroxide theories. According to the first theory, each hydrogen atom attached to a carbon atom is successively hydroxylated by the reacting oxygen. The second theory assumes that the oxygen and the hydrocarbon first form a peroxide, or moloxide (see Chapter 37) which is the active oxidizing agent. Experimental evidence has indicated that peroxide formation takes place with both saturated and unsaturated hydrocarbons. Peroxides of saturated hydrocarbons, however, apparently have not been isolated, but peroxides of unsaturated hydrocarbons have been obtained. They play an important rôle in the autoxidation of various petroleum distillates.

Ozone seems to react with saturated hydrocarbons in a manner similar to that of oxygen. With unsaturated compounds, however, it forms ozonides of definite composition, the ozone attaching itself to the molecule at the double bond. Decomposition of these ozonides is accomplished by heating or by hydrolysis, the resulting products usually being aldehydes or ketones.

As an oxidizing agent nitrogen dioxide reacts rather slowly with saturated hydrocarbons, forming monobasic acids, which can then be further oxidized. The oxidation proceeds eventually to oxalic acid and carbon dioxide. Simultaneously the nitrogen dioxide is reduced to nitric and nitrous oxides and ultimately to nitrogen.[10] The reactions are generally more easily effected with branched-chain than with straight-chain hydrocarbons. With olefinic hydrocarbons there are immediately formed the unstable isomeric nitrosates and pseudonitrosites, the formation often being accompanied by the polymerization of the olefin. With benzene in the cold, nitrogen dioxide slowly forms picric acid, and toluene is converted to trinitrotoluene. At the same time, toluene forms some nitronitrite compounds which may be decomposed by alkalies to yield various nitrocresols. In the presence of metallic salts such as aluminum or ferric chlorides, benzene forms addition products with nitrogen dioxide which can be decomposed by water.

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[7] *Cf.*, for example, Burmah Oil Co., British Patent 364,666, 1930; *Brit. Chem. Abs.* B, 1932, 299; French Patents 722,881 and 722,883, 1931; *Chem. Abs.*, 1932, **26**, 4170. Tesch, British Patent 370,367, 1929, (Void); *Chem. Abs.*, 1933, **27**, 2573. Limbach, *Petroleum Z.*, 1930, **26**, 683; *Chem. Abs.*, 1930, **24**, 4621.

[8] See, for example, Bataafsche Petroleum Maatschappij, British Patent 363,972, 1930; *Chem. Abs.*, 1933, **27**, 1744; Hausman, *loc. cit.*

[9] Abraham ("Asphalts and Allied Substances," D. Van Nostrand Co., New York, 1920) gives a comprehensive survey of the field. Pöll, *Erdöl und Teer*, 1931, **7**, 350; *Chem. Abs.*, 1932, **26**, 1426.

Electrolytic oxidation of petroleum hydrocarbons has been investigated to a limited extent.[11] The hydrocarbons are not conductors and must therefore be thoroughly emulsified with some electrolyte.[12] Low yields of products are usually obtained. Electrolytic oxidation and reduction appear to be more applicable to aromatic hydrocarbons, though even here these same objections hold.[13] Frequently with aromatics it is difficult to control the course of the reaction.

Other methods of oxidation are also available, though they probably have not been used to any great extent in commercial practice. Unsaturated compounds can be oxidized with neutral or alkaline solutions of potassium permanganate. This results in the addition of hydroxyl followed by the formation of acids, the latter step resulting in a rupture of the molecule at the double bond. Although saturated hydrocarbons are not generally oxidized under these conditions, nevertheless this reagent does attack them if they are mixed with unsaturated compounds.[14] Saturated hydrocarbons which contain tertiary carbon atoms appear to be oxidized in the presence of unsaturated hydrocarbons more readily than those containing secondary or primary carbon atoms.

The use of chromyl chloride as an oxidizing agent has been suggested. Etard[15] found that hexane from an American petroleum could be oxidized to yield a chlorohexyl ketone. Schulz[16] investigated the oxidizing effect of this reagent on various fractions of a Boryslaw oil but, although reaction products were obtained, no definite compounds were isolated. Generally the higher the specific gravity of the fraction, the greater was the yield of oxidized products. From the highest boiling fraction he obtained a small quantity of a substance which reacted with Fehling's solution and also reduced ammoniacal silver nitrate solution. All the oxidation products reacted with nitric acid to yield oily, noncrystallizable acids.

Petroleum hydrocarbons can be oxidized by passing their vapors over oxides of metals which are reducible or which exhibit more than one valence state. In this manner, Piotrowsky and Jakubowicz[17] increased the olefin content of various fractions of Boryslaw crude oil by treatment with manganese dioxide at 550° to 600° C. The fraction boiling between 50° and 150° C. was completely converted to unsaturated hydrocarbons.

Oxidation processes are generally aided by the presence of metals, metallic oxides, or their salts. Catalysts vary greatly in the way they influence the

[10] Schaarschmidt, *Z. angew. Chem.*, 1924, **37**, 933; *Chem. Abs.*, 1925, **19**, 942. See also, Schaarschmidt and Hofmeier, *Ber.*, 1925, **58B**, 1047; *Chem. Abs.*, 1925, **19**, 2634.

[11] See, for example, Chance, U. S. Patent 1,298,889, Apr. 1, 1919; Chapter 9.

[12] See, for example, Ges. für Chem. Ind., Norwegian Patent 27,389, 1916; *Chem. Abs.*, 1917, **11**, 236.

[13] See, for example, Soc. anon. pour l'ind. Chim. à Bâle, British Patent 15,750, 1915; *Chem. Abs.*, 1917, **11**, 1366.

[14] Kizhner, *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1788; *Chem. Abs.*, 1914, **8**, 911.

[15] *Ann. chim. phys.*, 1881, (5) **22**, 218; *Chem. Soc. Abs.*, 1881, **40**, 581.

[16] *Petroleum*, 1910, **6**, 189; *Chem. Abs.*, 1911, **5**, 587.

[17] *Petroleum Z.*, 1923, **19**, 5; *Chem. Abs.*, 1923, **17**, 1710.

oxidation of hydrocarbons. The specific catalysts suggested for a particular oxidation will be mentioned. Nevertheless, a few have been proposed for general oxidation reactions of hydrocarbons. Frazer,[18] for example, recommended finely divided porous manganese dioxide prepared by treating a manganese compound with cold nitric acid. Chromium-mixed catalysts obtained by heating salts such as basic zinc ammonium chromate, zinc tetrapyridine dichromate, and manganese ammonium chromate [19] have likewise been used for similar purposes, as well as ruthenium,[20] magnesium, nickel, molybdenum or tungstic oxides,[21] aluminum, tin, zinc, iron, cobalt, or nickel borates or phosphates treated with halogen, or halogen acids.[22]

Krauch [23] made the following partial general classification of catalysts: Carbon chains are split by vanadium, molybdenum, tungsten, uranium and their oxides. Copper, nickel, sulphur and selenium tend to promote dehydrogenation. Iron, though it lowers the cracking temperature and favors the dehydrogenation of both aromatic and hydroaromatic compounds, also promotes condensation reactions. Aluminum, which has been previously activated by treating it with solutions of certain metallic salts, often effects cleavage of the molecules at temperatures as low as 100° to 180° C. Aluminum chloride and boron trichloride, because of their polymerizing effect on olefinic hydrocarbons, are good catalysts for the manufacture of lubricating oils.[24] Antiknock compounds, such as lead tetraethyl and iron carbonyl, are classed as negative catalysts.

In this chapter are discussed some of the more general methods for the oxidation of petroleum hydrocarbons. Processes for the manufacture of specific compounds or for the oxidation of definite types of petroleum hydrocarbons are discussed in subsequent chapters.

OXIDATION OF GASEOUS HYDROCARBONS

Walter [25] obtained formaldehyde by the oxidation of 1 volume of natural gas, containing principally methane, with 5 volumes of air and 2 volumes of steam. Similarly, formaldehyde was obtained also from ethylene and air; a large excess of ethylene was required to prevent the occurrence of explosions. A number of metals and metallic oxides were employed as catalysts: platinum, iridium, silver, palladium, uranium, vanadium, manganese, copper, cobalt, nickel, thorium, titanium and tungsten; lead oxide either alone or mixed with aluminum oxide or calcium oxide; molybdic acid and thallium oxide, both of which were rather volatile and not easily separated from the products of the reaction; mercury and arsenic, though volatile also, could be easily separated from the reaction products.

According to Clancy,[26] a catalyst for the oxidation of methane may be prepared by heating the cyanamides of copper or silver to a temperature of 250° to 350° C. in the presence of the ferrocyanide or ferricyanide of bismuth, calcium, cerium, cobalt, vanadium or molybdenum.

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[18] U. S. Patent 1,602,404, Oct. 12, 1926; *Chem. Abs.*, 1926, **20**, 3786; *cf.* Frazer and Scalione, U. S. Patent 1,345,323, June 29, 1920; *J.S.C.I.*, 1920, **39**, 571A.

[19] Lazier, British Patent 301,806, 1927; *Brit. Chem. Abs.* **B**, 1929, 235; *cf.* British Patent 272,555, 1927; *Brit. Chem. Abs.* **B**, 1929, 163; both patents assigned to E. I. duPont de Nemours and Co., Inc.

[20] Badische Anilin- und Soda-Fabrik, German Patent 275,518, 1913; *Chem. Abs.*, 1915, **9**, 361.

[21] Charlot, *Compt. rend.*, 1933, 196, 1224; *Brit. Chem. Abs.* **A**, 1933, 680.

[22] I. G. Farbenindustrie A.-G., British Patent 325,234, 1928; *Brit. Chem. Abs.* **B**, 1930, 373.

[23] *Oil and Gas J.*, 1929, **27** (39), 156, 158, 160; *Chem. Abs.*, 1929, **23**, 2284.

[24] See Chapter 5.

[25] *J. pr. Chem.*, 1895, **51**, 107; German Patent 168,291, 1904; *Chem. Zentr.*, 1906, **1**, 1199; French Patent 360,785, 1905; *J.S.C.I.*, 1906, **25**, 493; British Patent 21,941, 1905; *J.S.C.I.*, 1906, **25**, 1173. See also Glock, German Patents 109,014 and 109,015, 1899; *Chem. Zentr.*, 1900, **2**, 304.

[26] U. S. Patent 1,425,576, Aug. 15, 1922; *Chem. Abs.*, 1922, **16**, 3369.

Sabatier and Mailhe[27] found that hydrocarbons of both the methane and ethylene series could be oxidized with air or oxygen at low temperatures in the presence of metallic oxides to yield aldehydes and acids. The oxidations were somewhat difficult to control because of the explosions which took place when the temperature of the catalyst reached the point of incandescence. Ethane can be oxidized to yield acetaldehyde. As a general rule, however, the resulting aldehyde contains one less carbon atom than the original hydrocarbon. From ethane, for example, was obtained mainly formaldehyde and from butane, propionic aldehyde. Acids are also formed, usually with fewer carbon atoms than the original hydrocarbon. Ethane, though it yields some acetic acid, is oxidized principally to formic acid.

The oxidation of hydrocarbons (such as those which occur in natural or refinery gases) chiefly to alcohols takes place in the presence of catalysts, under pressures of 1500 to 3500 pounds per square inch and at temperatures of 350° to 600° C., according to Young.[28] The quantity of oxygen in the gas mixture should be low, not exceeding 15 per cent. Numerous catalysts can be used in this process, as for example, manganese, silver wire, platinum foil, cobalt-plated copper wire, chromium-nickel alloy, and vanadium pentoxide powder. Beall[29] oxidized natural gas hydrocarbons with air by subjecting the mixture to a pressure of 300 to 1250 pounds per square inch and temperatures of 180° to 216° C. Platinum sponge or nitrogen oxides are employed as catalysts. The products are a mixture of aldehydes, ketones, acids and alcohols.

Oxygenated compounds are reported to be obtained when a mixture of methane and steam, together with carbon dioxide, hydrogen, or oxygen, is passed over metallic catalysts at 200° to 500° C., under pressures up to 500 atmospheres or more.[30] The oxygenated compounds so produced, which may be varied according to gaseous mixture used, are alcohols, aldehydes, ketones, and acids. Among the catalysts which can be used are zinc, magnesium, calcium, aluminum, chromium, manganese, vanadium, molybdenum, titanium, iron, cobalt, nickel and rare earths, or their compounds such as sulphides, arsenides, phosphates, silicates or borates. The catalysts may also contain various chromates, tungstates or molybdates. The apparatus may be of copper, or lined with copper, or made of steel containing vanadium, manganese, nickel or cobalt.

In a process developed by the I. G. Farbenindustrie A.-G., the catalytic oxidation of gases and vapors containing hydrocarbons of low molecular weight such as those obtained in the destructive distillation of coal yields acetic acid and its homologues, ketones, aldehydes, and alcohols together with propylene, butylene, butadiene and other olefins.[31] The hydrocarbon gases are mixed with gases such as carbon dioxide, steam or air, which supply oxygen for the reaction, and the mixture is subjected to a temperature of 500° to 800° C. in the presence of catalysts. These catalysts include manganese dioxide, vanadium oxide, the oxides of molybdenum, chromium, aluminum, and the carbonates of the alkali and alkaline earth metals. The olefins obtained in this process may be polymerized to substances of high molecular weight, for example, lubricants, or polymerization products which are either plastic or elastic.

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[27] *Compt. rend.*, 1908, **147**, 16; *Chem. Abs.*, 1908, **2**, 3057. *Compt. rend. des travaux présentés au Congrès du Clermont-Ferrand*, 1908, 1, 59.

[28] U. S. Patent 1,735,486, Nov. 12, 1929; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, **24**, 625; Standard Oil Development Co., British Patent 321,494, 1928; *Chem. Abs.*, 1930, **24**, 2755.

[29] U. S. Patent 1,859,193, May 17, 1932; assigned to J. C. W. Beall; *Brit. Chem. Abs.* **B**, 1933, 377. See also *Refiner*, 1932, **11**, 422; *Chem. Abs.*, 1932, **26**, 6108.

[30] Dreyfus, British Patent 337,410, 1929; *Chem. Abs.*, 1931, **25**, 2152.

[31] I. G. Farbenindustrie A.-G., British Patent 305,603, 1927: *Brit. Chem. Abs.* **B**, 1929, 275; French Patent 654,316, 1928; *Chem. Abs.*, 1929, **23**, 3796.

Burke and Fryling[32] effected selective oxidation of hydrocarbons in the absence of a catalyst. They state that the temperature must be carefully controlled, being kept at a point where only partial oxidation takes place and any hydrogen or carbon monoxide present are unaffected. This temperature is generally about 350° C. An aluminum reaction chamber is employed (aluminum having no catalytic action), and a pressure of more than 300 pounds per square inch is maintained.

OXIDATION OF LIQUID HYDROCARBONS IN THE VAPOR PHASE

Reactions which occur in the oxidation of hydrocarbons in the vapor phase are very sensitive to temperature, time of contact, pressure and proportion of constituents in the reaction zone.[33] Continuous recirculation is advantageous in processes of this kind. Marek[34] observed that aliphatic hydrocarbons require lower temperature, shorter contact time and lower oxygen concentration than aromatics. Increased pressures reduce the temperatures required for oxidation and stabilize the products but they also increase the possibility of explosion.

In carrying out the oxidation of hydrocarbons to alcohols, acids, aldehydes, and other products, Frolich[35] heated the mixture of air and hydrocarbon to temperatures between 350° and 700° C., at pressures between 70 and 250 atmospheres. Thus, in the oxidation of butane with air, a mixture of the two gases is passed through a chamber partly filled with nickel catalyst. The pressure is maintained at 160 atmospheres and the temperature at 430° C. The products consist of ethyl and propyl alcohols, acetic acid and esters, with smaller proportions of acetaldehyde and propionaldehyde, acetone, and methyl and butyl alcohols.[36] Similar methods have been proposed by Pugh, Tauch and Warren,[37] Lewis,[38] and Dearborn and Gray.[39] Low molecular weight organic acids or anhydrides such as acetic anhydride, can be mixed in as diluents to avoid danger of explosion.[40]

For the oxidation of gasoline vapors, Freund[41] employed an iron tube packed with petroleum coke (which had been previously ignited) and conducted the mixture of gasoline vapors and air through this tube at temperatures of 400° to 500° C. Two samples of gasoline were used: A Galician gasoline from Boryslaw crude oil (predominantly paraffinic in character), and a cracked gasoline (having a high content of unsaturated hydrocarbons) made from a crude oil obtained in the western part of the United States. Oxidation was found to increase with rising temperatures. It was also increased by prolonging the time of passage of the gases through the tube and by using a larger proportion of air in the gas mixture. With four successive passages of a given quantity of gasoline vapor through the tube at 400° C., about 30 per cent was converted into oxidation products, which included acids, phenols and other aromatic bodies, together with unsaturated compounds, esters, water and carbon dioxide. Under the same conditions the American gasoline, because of its unsaturated character, yielded a larger proportion of oxidation products than the Galician gasoline. A relatively large amount of acetic acid was found among the oxidation products of the American gasoline. Purely pyrolytic reactions were shown to take place by substituting nitrogen for the air, a larger proportion of unsaturated hydrocarbons being thus formed.

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[32] U. S. Patent 1,911,746, May 30, 1933; assigned to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 3941.

[33] Beall, *Refiner,* 1932, 11, 463,495; *Chem. Abs.*, 1932, **26**, 6108; Wilken-Jorden, *J. Chem. Met. Mining Soc. S. Africa,* 1932, **32**, 248; *ibid.*, 1932, **33**, 203; *Chem. Abs.*, 1932, **26**, 4941; *ibid.*, 1933, **27**, 3065.

[34] *Ind. Eng. Chem.*, 1932, **24**, 1103.

[35] U. S. Patent 1,858,822, May 17, 1932; *Chem. Abs.*, 1932, **26**, 3803; British Patent 341,130, 1929; *Brit. Chem. Abs.* **B**, 1931, 333; German Patent 554,780, 1929; *Chem. Abs.*, 1932, **26**, 5963; French Patent 682,979, 1929; *Chem. Abs.*, 1930, **24**, 4519; all patents assigned to Standard Oil Development Co. See also, Frolich and Wiezevich, *Ind. Eng. Chem.*, 1932, **24**, 13.

[36] *Cf.* also Young, U. S. Patent 1,735,486, Nov. 12, 1929; *Chem. Abs.*, 1930, **24**, 625.

[37] U. S. Patent 1,812,714, June 30, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**. 1932, 635.

[38] U. S. Patent 1,870,816, Aug. 9, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1932, **26**, 5738.

[39] U. S. Patent 1,861,956, June 7, 1932; assigned to The Texas Company.

[40] Luther and Klein, German Patent 572,896, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4238.

[41] *Z. angew. Chem.*, 1927, **40**, 368; *Chem. Abs.*, 1927, **21**, 2117.

Employing a somewhat lower temperature (250° C.), Cândea[42] observed the formation of aromatic compounds when the vapors of Rumanian gasolines (which boiled up to 150° C.) and air were passed over a catalyst. Iron oxide (Fe_2O_3) appeared to be the best catalyst and the highest yield of aromatics obtained was 6.4 per cent. This reaction appears to be dehydrogenation, other examples of which are discussed in Chapter 39.

Results on the vapor phase oxidation of hydrocarbons have been reported by Shimose.[43] In his work he found that maleic acid (together with some carbon dioxide and formaldehyde) was the principal product of the oxidation of n-pentane, n-heptane, n-octane, 2-amylene, 2-isoamylene, diisoamylene and cyclohexane with air. The same substances were also obtained by the oxidation of gasoline vapors. The catalysts used were the oxides and salts of vanadium, molybdenum, uranium, chromium and manganese.

To obtain oxidation products from petroleum hydrocarbons with boiling ranges higher than those of gasoline, two general methods have been used: (1) the direct oxidation of the hydrocarbons in the vapor phase, and (2) the cracking of such hydrocarbons followed by the vapor phase oxidation of the lower-boiling products thus formed.

Walter[44] oxidized a petroleum distillate boiling above 300° C. by passing the vapors together with air and steam over a heated catalyst of copper deposited on asbestos. The products of the reaction were acetic acid and its homologues, and aldehydes.

James[45] produced aldehydes and aldehyde-acids by the passage of a mixture of hydrocarbon vapors and air through a heated reaction zone containing catalysts. The temperature of the reaction zone varied from 230° to 500° C., being determined by the type of petroleum distillate undergoing oxidation. Steam may be used as a diluent for the gas mixture. Catalysts used included the oxides of metals which are capable of exhibiting more than one valence state, as for example, molybdenum, vanadium, and uranium. In carrying out the process, the oil and air are both led into a heating and mixing vessel. The heated mixture of hydrocarbon vapors and air is then passed through a screen of the catalytic material and from there into a condenser. The time of contact of the vapors with the screen is of the order of 0.3 second.

For example, when a mixture of air and the vapors of a Pennsylvania petroleum fraction, 90 per cent of which distilled between 250° and 324° C., was conducted over a molybdenum oxide catalyst at a temperature of 310° to 320° C., the condensate was reported to consist of 28 per cent by volume of aldehydes and 46 per cent by volume of aldehyde-acids.[40] The portion of such condensates boiling up to 300° C. could be mixed with benzol, alcohol or gasoline and used as a motor fuel. The soaps obtained by extracting portions boiling above 300° C.

[42] *Mon. pétrole Roumain*, 1924, **23**, 1295; *Chem. Abs.*, 1924, **18**, 3472.

[43] *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1931, **15**, 251; *Chem. Abs.*, 1931, **25**, 4694.

[44] *Loc. cit.*

[45] U. S. Patent 1,697,653, Jan. 1, 1929; *Chem. Abs.*, 1929, **23**, 1136; Reissue 18, 522, July 12, 1932; *Chem. Abs.*, 1932, **26**, 4611. U. S. Patent 1,716,272, June 4, 1929; see also Byrnes, British Patent 138,113, 1920; *J.S.C.I.*, 1921, **40**, 636A; British Patent 209,128, 1922; *Chem. Abs.*, 1924, **18**, 1565.

[46] James, U. S. Patent 1,697,653, Jan. 1, 1929.

with sodium or potassium hydroxide solutions exhibited detergent properties. The corresponding calcium and aluminum soaps were considered appropriate for water-proofing materials. The residue, after the alkali-extraction, contained alcohols, aldehydes and waxes and was said to be utilizable for a lubricant. Either before or after the removal of the aldehyde-acids with alkaline solutions, the product was stated to be thickened or resinified by dry hydrogen chloride, anhydrous zinc or calcium chloride, or phosphoric acids. These resinous substances were acidic in nature and could be converted into calcium or sodium soaps.[47]

The separation of the aldehydes and aldehyde-acids obtained in this process may be effected by converting the acids to salts, for example, the insoluble calcium salts.[48] After separation of the acids, the residual aldehydes and hydrocarbons can be returned to the system for further oxidation. Any unsaturated oxygenated product can be converted to the corresponding saturated compound by hydrogenation or halogenation.[49]

The operation of a plant for the oxidation of petroleum vapors on a commercial scale has been described by Bitler and James.[50]

Other methods have been suggested for the oxidation of petroleum vapors. For instance, Martin[51] oxidized the vapors by mixing them with oxygen and subjecting the mixture to the influence of ultraviolet light. The products, after being condensed, are stated to be usable as frothing agents. Egloff and Morrell[52] suggested conducting the mixture of hydrocarbon vapors and oxidizing gas through a heated zone in which the mixture is subjected to a high-potential electrical discharge under pressure. With some types of hydrocarbon vapors, the presence of aluminum chloride or ferric oxide promotes the reaction. The use of oxidizing gases such as air, oxygen, ozone and the oxides of nitrogen, leads to the production of oxygenated compounds such as alcohols, aldehydes, ketones and acids.

The second method of obtaining oxidation products from petroleum hydrocarbons, that is, cracking the distillate and then oxidizing the lighter products is exemplified by the processes developed by Ellis. In one procedure he[53] cracked kerosene, for example, at 800° to 900° C., under a pressure of 10 to 20 atmospheres, obtaining lighter products with a large content of aromatics. These lighter products, together with air possessing a constant moisture content, are passed over a catalyst kept at 300° to 400° C. Chromium oxide, vanadium oxide, molybdenum oxide, iron chromate and similar compounds supported on a carrier such as asbestos or pumice serve as catalysts. The volume of oxygen used is such that the oxygen content of the gas mixture is about 20 per cent, which is very much less than that required for complete combustion. The oxidation products are passed through an air condenser which allows separation of the higher boiling constituents, then through a scrubbing tower in which the water-soluble products are collected, and finally through oil scrubbers. The aqueous solution from the scrubbing tower contains not only monobasic acids such as acetic acid and its homologues, but also dibasic acids. When the kerosene, however, is cracked at slightly lower pressures (at 4 to 5 atmospheres) and the catalyst is maintained at slightly higher temperatures (400° to 500° C.) for example, in addition to organic acids there are also obtained aldehydes or aldehyde-acids.[54]

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[47] Byrnes, British Patent 173,750, 1921; *Chem. Abs.*, 1922, **16**, 1503.

[48] James, U. S. Patent 1,681,185, Aug. 21, 1928; *Chem. Abs.*, 1928. **22**, 3667. See also U. S. Patent 1,753,517, Apr. 8, 1930; *Chem. Abs.*, 1930, **24**, 2591. French Patent 520,828, 1921. U. S. Patent 1,912,484, June 6, 1933; *Chem. Abs.*, 1933, **27**, 4239.

[49] James, U. S. Patent 1,681,238, Aug. 21, 1928; *Chem. Abs.*, 1928, **22**, 3667.

[50] *Chem. Met. Eng.*, 1928, **35**, 156.

[51] U. S. Patent 1,678,403, July 24, 1928; assigned to Minerals Separation North American Corp.; *Chem. Abs.*, 1928, **22**, 3523; *cf.* also U. S. Patent 1,510,150, Sept. 30, 1924.

[52] U. S. Patent 1,710,155, Apr. 23, 1929; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1929, **23**, 2820.

[53] U. S. Patent 1,516,720, Nov. 25, 1924; assigned to Ellis-Foster Co.; *J.S.C.I.*, **1925**, 64B.

Ellis[55] found that the oxidation proceeds more slowly and can be controlled more readily if the hydrocarbon-air-water vapor mixture is cooled just before it enters the reaction chamber so that it comes in contact with the catalysts as a mist. This method of oxidation of hydrocarbon vapors, particularly those from cracking petroleum products, leads to the formation of aromatic derivatives, especially phthalic anhydride. The yield of the latter depends to a large degree upon the proportion of naphthenes present in the original oil. Extraction of the original oil with alcohols, sulphur dioxide, or other solvents at low temperatures makes it possible to separate many of the paraffin hydrocarbons. Such extracted oils, containing a higher proportion of naphthenes, give on oxidation a larger yield of aromatic derivatives.

With silver, copper, or aluminum, a temperature between that of black and dull red heat, (that is, slightly below 538° C.) aldehydes are the predominating reaction products.[56] Gases such as carbon dioxide can be used as well as air. Formaldehyde is the principal aldehyde formed, together with small quantities of acetaldehyde, acrolein and benzaldehyde. The small quantities of acids produced consist mainly of formic, propionic, benzoic, citraconic, maleic, and phthalic acids.

In oxidizing gaseous products which contain a large percentage of unsaturated compounds (20 per cent or more) obtained in the cracking of petroleum distillates, Ellis[57] found that, by carefully regulating the quantity of air used, it is possible to obtain monobasic acids such as acetic, propionic, and butyric. Increasing the quantity of air results in the production of oxalic, succinic, malic, maleic, and similar dibasic acids. During oxidation the temperature of the catalyst should be kept between 400° and 500° C. It is possible, however, to carry out the oxidation at lower temperatures provided the pressure is greatly increased.

In a process developed by Palmer[58] the oil or gas is first cracked to yield more active hydrocarbons, that is, unsaturated hydrocarbons. These are partly oxidized with steam, air, or oxygen in the presence of a catalyst (platinum or vanadium on asbestos) at 300° to 700° C. After the precipitation of tar, the products are recovered and partially separated in a series of condensers. Aldehydes appear to be the main oxidation products. The residual gases can be used for the production of carbon black.

Oxidation during cracking, however, can be made so extensive that carbon monoxide and dioxide, nitrogen and hydrogen result.[59] Thus, gas oil, when mixed with air and steam and cracked in the presence of an iron-chromium alloy, yields these gases. The greater part of the carbon monoxide is then oxidized to carbon dioxide by passing the gas mixture over a ferric oxide catalyst. The remaining carbon monoxide is oxidized by adding the requisite quantity of air and conducting the gaseous mixture over mixed oxides of iron and chromium capable of preferentially oxidizing the carbon monoxide. The carbon dioxide is removed with alkaline solutions and the resulting mixture of hydrogen and nitrogen can be used for the production of ammonia.[60]

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[54] Ellis, U. S. Patent 1,697,264, Jan. 1, 1929; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1259.

[55] U. S. Patent 1,697,262, Jan. 1, 1929; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1259; U. S. Patent 1,697,263, Jan. 1, 1929; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1259.

[56] Ellis, U. S. Patent 1,697,265, Jan. 1, 1929; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1259.

[57] U. S. Patents 1,697,266 and 1,697,267, Jan. 1, 1929; both assigned to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1259.

[58] U. S. Patent 1,699,627, Jan. 22, 1929; *Chem. Abs.*, 1929, 23, 1260.

[59] Nitrogen Corporation, British Patent 163,703, 1921; *Chem. Abs.*, 1922, 16, 799.

[60] The production of hydrogen by the action of steam on saturated hydrocarbons is discussed in Chapter 10.

OXIDATION IN THE LIQUID PHASE

The methods for oxidizing liquid hydrocarbons may be grouped into three main divisions: (1) oxidation during distillation, (2) oxidation at high temperatures (about 400° C.) while keeping the liquid under pressure, and (3) oxidation at relatively low temperatures (about 200° C.) and under atmospheric or slightly increased pressure. The first two methods are, of course, applicable to nearly all types of distillates, but the last method can be used only with high-boiling distillates. Heat is evolved during the oxidation of the hydrocarbons.

LIQUID-PHASE OXIDATION DURING DISTILLATION

In the Dubbs[61] process, oil is heated in a still to a temperature somewhat lower than its boiling point and air is introduced through a perforated pipe near the bottom of the still. After the reaction has started, the heat generated is sufficient to maintain the temperature and cause distillation of the lighter hydrocarbons formed. This process is essentially a dehydrogenation, the temperature being so regulated that hydrogen of the hydrocarbon combines with the oxygen. If steam is introduced with the air, discoloration of the residue in the still is prevented to a large degree.

A similar process has been proposed by the Société Anonyme des Combustibles Industriels[62] for the oxidation of hydrocarbons such as coal tar, wood tar, and schist oils. Air enriched with oxygen or ozone can be used in the oxidation, the heat generated being sufficient for continuing the process. The distillates are said to be usable as lubricating oils. The temperature of distillation can be lowered, of course, by reduction of pressure.

The production of mineral frothing agents is accomplished by oxidizing petroleum distillates in the presence of carbon. Martin[63] passes the oil and air over heated coke or charcoal in a retort and condenses the vapors in a series of condensers. A temperature of 400° C. is used when the oxidation is carried out in the presence of coke, and 350° C. with charcoal. The oily product which separates in the condensers can be employed as a frothing agent. Steam or water is introduced at the beginning of the operation to minimize the danger of explosions. An excessive quantity must be avoided as the condensed oxidation products easily form emulsions with water which are difficult to separate.

In the process developed by Brewster[64] the oil is maintained at the conversion temperature (380° to 405° C.) under a pressure of 4 to 5 atmospheres and air is supplied to the still. The evolved vapors are passed through a stripping column in countercurrent heat exchange with incoming oil which is thus preheated. The condensed heavier fractions are returned to the still.

LIQUID-PHASE OXIDATION AT HIGH TEMPERATURES AND PRESSURES

An example of liquid-phase oxidation at high temperatures and pressures is the Penniman[65] process. Crude petroleum, or its distillates, is mixed with powdered coal, coke or peat, and then oxidized by passing air through a heated body of the material. With gas oil, for example, the oil is first heated in a still to 260° C. (500° F.) under a pressure of 20 atmospheres. On introduction of air the temperature rises to 385° to 400° C. (725° to 750° F.). The distillate obtained during oxidation separates on standing into an upper water-insoluble layer, an intermediate layer, and a lower aqueous solution of organic acids. Acids, phenols and aldehydes may be extracted (in that order) from the upper layer with solutions of sodium carbonate, sodium hydroxide and sodium bisulphite, respectively. The residue from the upper layer is washed with water, treated with sulphuric acid, and then distilled to yield a motor fuel. The residue is returned to the oxidation still. From the acid extract, alcohols can be obtained by diluting with water and distilling.

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[61] U. S. Patent 1,100,717, June 23, 1914; *Chem. Abs.*, 1914, 8, 2942.

[62] British Patent 16,182, 1905; also French Patent 349,214, 1905; *J.S.C.I.*, 1905, 24, 686.

[63] U. S. Patent 1,510,150, Sept. 30, 1924; assigned to Minerals Separation North American Corp.; *Chem. Abs.*, 1925, 19, 29.

[64] U. S. Patent 1,694,092, Dec. 4, 1928; assigned to Standard Oil Co. of California; *Brit. Chem. Abs.* B, 1929, 234.

[65] British Patent 252,327, 1925; *Chem. Abs.*, 1927, 21, 1546. British Patent 255,020, 1925; *Chem. Abs.*, 1927, 21, 2793; British Patent 256,922, 1925; *Chem. Abs.*, 1927, 21, 3126; British Patent 257,886, 1925; *Chem. Abs.*, 1927, 21, 3123.

The lower aqueous layer obtained in the Penniman process contains acids (principally acetic) and aldehydes (largely acetaldehyde and propionic aldehyde) together with some ketones and alcohols. On distillation this layer yields acetaldehyde and a liquid which can be either added to a motor fuel to increase its antiknock properties or used as a solvent for shellac and other resins. The distillation residue, after treating it with sulphuric acid, is steam-distilled to obtain gums.

An examination of the aqueous distillate obtained in the oxidation of a Mid-continent gas oil distillate by air, using the Penniman process, was made by Swann, Howard and Reid.[66] The aqueous distillate was separated into several fractions which were examined individually. An estimate of the quantities of organic substances in the water layer, per 1000 pounds of gas oil oxidized, was as follows:

Acetaldehyde	5.5 lbs.	Ethyl alcohol Ethyl acetate	2 lbs.
Acetone Methyl acetate Methanol Dimethyl acetal	19 lbs.	Allyl alcohol	3.5 lbs.
		Acetic acid	7 lbs.

These quantities would, of course, vary considerably with different operating conditions. Aluminum chloride, or the oxides of manganese, lead, iron, chromium, vanadium, zinc, copper, or calcium may be used as catalysts.

In the Cross[67] process, the oil is heated to the conversion temperature and conveyed to a reaction chamber, the pressure being maintained at 400 to 750 pounds. On the introduction of air or other oxidizing gas into the reaction chamber a considerable rise in temperature results. From the reaction chamber the oil passes to a still kept under reduced pressure. The evolved vapors are then fractionated.

Luther and Wille[67a] proposed to eliminate the formation of resinous by-products in the oxidation of hydrocarbons in the liquid phase by stopping the reaction before oxidation is complete, removing the products by extraction with methyl alcohol, and continuing the oxidation of the residue.

A procedure in which heated air is passed through a nozzle into a low gravity oil, contained in a closed tank, has been developed by Persch.[68] The air is forced into the oil in such a manner that the oil is atomized. The low-boiling products formed are condensed, flow back into the tank, and promote contact between the gas and the particles of atomized oil. After the oil has been sufficiently acted upon, the low-boiling products are separated by distillation with a current of air. A breaking-down of the complex hydrocarbons and their recombination in different proportions is said to be the mechanism of this process, the oxygen of the air probably assisting in the rearrangement.

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[66] *Ind. Eng. Chem.*, 1931, **23**, 1277.

[67] U. S. Patent 1,696,030, Dec. 18, 1928; assigned to Gasoline Products Co.; *Chem. Abs.*, 1929, **23**, 968.

[67a] German Patent 524,354, 1925; *Chem. Abs.*, 1931, **25**, 3664; French Patent 680,351, 1929; *Chem. Abs.*, 1930, **24**, 3798; both patents assigned to I. G. Farbenindustrie A.-G.

[68] U. S. Patent 1,453,479, May 1, 1923; *Chem. Abs.*, 1923, **17**, 2189.

LIQUID-PHASE OXIDATION AT RELATIVELY LOW TEMPERATURES AND PRESSURES

The blowing of petroleum residues converts them into asphaltic products with high melting points and viscosities and of good ductility. In one process[69] high pressure air or steam or both is introduced into a still through a number of pipes extending to the bottom. The pipes are arranged in such a manner that a double circulatory motion of the residue in the still is obtained. Light volatile products which are formed are taken off at the top. The condensed vapors may be returned to the oil undergoing oxidation.[70] The residues from cracked distillates are oxidized under reduced pressure by steam or air-blowing at 300° C.[71] Bauer and Urman[72] report that if the hot products are treated with super-heated steam or an indifferent gas, directly after oxidation, an improvement in quality is obtained.

MacLachlan[73] oxidized petroleum residue or heavy hydrocarbons mixed with natural or prepared asphalt by continuously circulating oxidizing gases and resulting fumes through the charge. Small additions of air or other oxidizing gas are continually made to replace that used in the oxidation.

Rudigier[74] proposed the introduction of hot petroleum residuum, at a temperature of 215° to 225° C. (420° to 440° F.) into a tank. Air is admitted at the bottom of the tank through a perforated pipe. The temperature during oxidation rises to about 235° C. (456° F.). Any volatile products formed during oxidation are passed through a scrubbing tower and washed with a water spray. The wash water together with the entrained distillate is then run to a separator where the hydrocarbons are recovered.

Distillation of volatile products during oxidation can be prevented by mixing petroleum residuum with a high-boiling coal tar and oxidizing at low temperatures.[75] For example, the process can be started at 110° C. and finished at 220° C., the air being forced through the mixture at such a rate that all of the oxygen is absorbed. The operation can be made continuous by connecting several oxidation chambers in series so that any chamber can then be shut off, the charge withdrawn, and a fresh charge introduced.

For the production of materials with rubber-like properties, Kirschbraun[76] conducted petroleum residuum together with air through a long pipe coil in which the temperature is gradually increased from 200° to 350° C. It then passes into a receiving tank where, after agitation, the liquid oxidized asphalt is withdrawn.

An apparatus in which the oxidation of heavy oils and pitches may be effected has been described by Gevers-Orban.[77] It consists of a cylindrical horizontal tank fitted with a horizontal shaft provided with paddles. An inlet nozzle for admitting the oxidizing gas is placed at one end near the top of the tank, and a connection is provided at the other end for leading the exit gases to a condenser. Heat is applied externally. With a tank about half full of oil, the rotation of the paddles throws a spray of oil into the upper part. The oil is thus brought into intimate contact with the oxidizing gas. The more volatile constituents pass into the condenser and are recovered. As oxidation continues, the oil remaining in the tank becomes thicker.

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[69] Black and Rial, U. S. Patent 1,718,679, June 25, 1929; assigned to Pan American Petroleum Co.; *Chem. Abs.*, 1929, 23, 4060.

[70] Gard and Subkow, U. S. Patent 1,911,114, May 23, 1933; assigned to Union Oil Co. of Calif.; *Chem. Abs.*, 1933, 27, 4072.

[71] Sakhanov and Logvinova, *Grozni Neft.*, 1931, 1 (6-7), 69; *Brit. Chem. Abs.* B, 1932, 1065.

[72] Austrian Patent 118,641, 1930; assigned to Galicyjskie Towarzystwo Naftowe "Galicja" Sp. Akc.; *Chem. Abs.*, 1930, 24, 5478.

[73] U. S. Patent 1,774,756, Sept. 2, 1930; *Brit. Chem. Abs.* B, 1931, 471.

[74] U. S. Patent 1,673,533, June 12, 1928; assigned to Standard Development Co.

[75] Hennebutte, U. S. Patent 1,044,175, Nov. 12, 1912; *Chem. Abs.*, 1913, 7, 250; Canadian Patent 143,156, 1912; *Chem. Abs.*, 1913, 7, 415.

[76] U. S. Patent 1,715,069, May 28, 1929; one-half assigned to Belknap; *Chem. Abs.*, 1929, 23, 3571.

[77] U. S. Patent 1,404,435, Jan. 24, 1922; *Chem. Abs.*, 1922, 16, 1147. See also Soc. Anon. Cava., German Patent 257,963, 1913; *Chem. Abs.*, 1913, 7, 2681.

Petroleum residues can also be oxidized by causing the material to flow through a series of three cylindridal receivers countercurrent to a stream of air or air containing oxygen or ozone.[78] No external heat is required inasmuch as oxidation proceeds with the generation of heat, which may be conserved by passing the gas directly from one receiver into another. With a partial vacuum, the latent heat of evaporation alone is sufficient to effect both dehydration of the tar and distillation of low-boiling hydrocarbons. The substances carried away by the gases can be condensed by passing them into cold tar or into vessels immersed in cold tar which is later treated.

Turek[79] found that tars or pitches which could not be used satisfactorily for the manufacture of artificial asphalts by blowing with air or oxygen were rendered adaptable if mixed with phenolic tars in such proportions that the resulting mixture had a phenol content of 12 to 24 per cent. This mixture can be oxidized with heated air in the presence of ferric oxide containing some sulphur.

In an oxidation process developed by Mann and Chappell[80] heated petroleum oil, together with air, is passed over the suboxides of nickel, iron, or copper to produce aromatic compounds such as benzene, toluene and xylene. Mann and Chappell used temperatures which vary from 600° to 750° C. These are considerably higher than the temperatures employed in other processes mentioned in this section. They maintain the pressure at slightly less than 1 atmosphere. The proportions of air required vary from 500 to 800 cubic feet for each 15 to 20 gallons of oil. The main reaction involved is considered to be a dehydrogenation. Conversion of 20 to 45 per cent of the oils to permanent hydrocarbon gases, and 40 to 75 per cent to aromatic hydrocarbons is said to be secured.

The judicious use of oxidation or blowing is generally found to be the most desirable method of finishing petroleum asphalts, particularly those produced in pipe stills. There appears to be considerable need, however, for an investigation of the reactions which take place when various asphalt stocks are subjected to blowing. Some theoretical reactions have been hazarded but few detailed investigations have been conducted. It has never been definitely proven under what condition, if at all, oxygen is added to the hydrocarbons in the finished asphalt, or whether the process is one of dehydrogenation. The products obtained by blowing a poorly stripped asphalt differ in physical characteristics from those of an asphalt which has been carefully stripped of heavy oils. When such reactions are more thoroughly understood it may be possible to correlate them directly with the adaptability of asphalts for various purposes.[81]

[78] Rosen, British Patent 10,208, 1913; *Chem. Abs.*, 1914, 8, 3501. See also The Engineering Fuel and Co., Japanese Patent 32,121, 1918; *Chem. Abs.*, 1918, 12, 2247.

[79] Turek, Austrian Patent 110,401, 1928; *Chem. Abs.*, 1929, 23, 1263.

[80] U. S. Patent 1,214,204, Jan. 30, 1917; assigned to Standard Oil Co. of California; *Chem. Abs.*, 1917, 11, 1039.

[81] Hubbard, *J.S.C.I.*, 1929, 48, 108T. Hugel and Frangopol (*Ann. Office nat. Combust. liq.*, 1932, 7, 225, 417; *Brit. Chem. Abs.* B, 1933, 659) reported the presence of polycyclic hydrocarbons in Saar pitch. Lahocinski (*Przemysl Naftowy*, 1933, 8, 229; *Chem. Abs.*, 1933, 27, 4065) investigated the change in the asphaltene, resin, oil, and wax content of asphalts during oxidation.

MISCELLANEOUS PROCESSES

Egloff and Morrell[82] produced a liquid of lower boiling range together with oxidation products (aldehydes, alcohols, ketones and acids) by heating a petroleum oil in the presence of metallic oxides such as copper oxide or barium peroxide in a still under pressure to a temperature sufficient to cause vaporization. The vapor which is evolved is separated into lighter and heavier fractions. The latter, after condensation, are treated with an oxidizing gas (air, oxygen, ozone, or the oxides of nitrogen) and then returned to the still. Hydrogen, carbon monoxide and nitrogen are the products of oxidation of methane or natural gas with the oxides of chromium, titanium, tungsten and molybdenum at 800° to 1000° C.[83] Each of these metals are capable of forming several higher oxides which are stable to hydrogen under the working conditions. The reduced oxide is reconverted to the higher oxide by treating with air, steam or carbon dioxide.

Herrmann and Baum[84] oxidized petroleum oil by burning a flame of oxygen and hydrogen (or other combustible gas) beneath the surface of the liquid. When the temperature of the liquid near the flame becomes high enough to allow it to burn with oxygen alone, the flow of hydrogen is discontinued. Ethylene and acetylene are formed together with liquid and gaseous products due to the cracking of the petroleum oil by heat liberated by the flame. Reaction may be accelerated by dissolving or suspending catalytic material in the liquid or using such materials in the construction of the burner. This procedure is said to be applicable to the decomposition of other organic liquids, e.g., alcohols.

For the oxidation of liquid hydrocarbons Esmarch[85] proposed treating oils with air between the closely adjacent surfaces of water-cooled electrodes which produce high-frequency corona arc discharges.

Since alcohols are frequently obtained in the oxidation of petroleum hydrocarbons some mention of the oxidation of these substances would not be out of place. Sabatier and Mailhe[86] studied the oxidation of primary alcohols in the presence of oxides, particularly those of silicon, molybdenum, and tungsten, at temperatures between 250° and 350° C. At 300° C. some carbon dioxide was obtained in addition to aldehydes and acids. At about 350° C. those oxides which were not easily reduced by the alcohol vapors caused the oxidation to proceed in one of three ways: to form (1) aldehydes and hydrogen; (2) water and unsaturated hydrocarbons; or (3) to cause both of these reactions (1 and 2) to take place simultaneously. At this same temperature oxides of the type represented by cadmium or stannous oxide, which are only slowly reduced by the alcohol vapors, reacted very much like the non-reducible oxides. In the presence of easily reducible oxides, however, the alcohol vapors were oxidized with the formation of carbon dioxide.

The indirect oxidation of olefins to ketones, through the intermediate formation of alcohols, has been proposed by Ellis and Wells.[87] Light hydrocarbon gases obtained in the cracking of heavy petroleum distillates are absorbed in sulphuric acid which has a specific gravity of about 1.8. The acid extract is diluted with twice its volume of water and distilled. The alcohols collected are treated with a mild oxidizing agent such as sodium dichromate, and the ketones are removed by distillation. The rectified ketones can be used as solvents. The olefin gases can be absorbed in the acid and the acid extract oxidized directly, thus omitting one distillation step (that in which the alcohols are separated). In place of dichromates, other oxidizing agents such as nitric or hypochlorous acid can be used in the presence of catalysts.

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[82] U. S. Patent 1,733,656, Oct. 29, 1929; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1930, 24, 495.

[83] I. G. Farbenindustrie A.-G., British Patent 360,081, 1930; *Brit. Chem. Abs.* **B**, 1932, 62.

[84] U. S. Patent 1,864,196, June 21, 1932; assigned to Consortium für Elektrochemische Industrie; *Chem. Abs.*, 1932, 26, 4347. See also Chapter 45.

[85] U. S. Patent 1,708,126, Apr. 9, 1929; assigned to Siemens and Halske A.-G.; *Chem. Abs.*, 1929, 23, 2567.

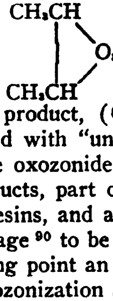
[86] *Compt. rend.*, 1908, 147, 16; *Chem. Abs.*, 1908, 2, 3057. *Compt. rend. des travaux présentés au Congrès du Clermont-Ferrand*, 1908, 1, 59.

[87] U. S. Patent 1,450,493, Apr. 3, 1923.

Faber[87a] described a method of "reforming" natural gases, which consists of a partial combustion of the gases with air at a temperature between 540° and 925° C. Other examples of similar processes have already been mentioned in Chapters 8 and 10.

OXIDATION WITH OZONE

Ozone is sometimes used in the oxidation of hydrocarbons, and as frequent examples of this type of oxidation are given in the following chapters, it need only be briefly mentioned at this point. Ozone is generally mixed with oxygen for the oxidation of unsaturated compounds, such substances reacting with ozone to form ozonides which can be decomposed, by heat or hydrolysis, to yield aldehydes, ketones and acids (see Chapter 38). The reaction of unsaturated hydrocarbons with ozone has been used to determine the number of double bonds in the molecule.[88]

Harries[89] has shown that oxozone (O_4) is present in ordinary ozone (O_3), hence this may often lead to conflicting results. Oxozone may be eliminated by washing the ozone mixture with sulphuric acid and with sodium hydroxide. 2-Butene, for example, when treated with "washed" ozone yields the normal ozonide,  $CH_3CH\cdot O_3\cdot CHCH_3$, (which can be distilled *in vacuo*), together with a sirupy dimeric product, $(C_4H_8O_3)_2$ (which is not distillable). When the same olefin is treated with "unwashed" ozone the normal ozonide is again obtained together with the oxozonide, $C_4H_8O_4$, and the viscous dimeric product, $(C_4H_8O_4)_2$.

Products, part of which are said to be substitutes for turpentine and linseed oil or resins, and another part of which can be used as motor fuel, are reported by Ramage[90] to be obtained by ozonizing at a temperature of 30° to 40° C. below its boiling point an olefin fraction boiling at 125° to 250° C. The vapors evolved during ozonization are condensed for use as a motor fuel. Ozonization is stopped when the material reaches a specific gravity of 1.16. This material is intended as a substitute for linseed oil. If during ozonization the vapors are returned to the still by means of a reflux condenser then only a turpentine substitute is obtained. Further ozonization of this product yields resinous bodies.

Kita, Abe and Tada[91] studied the effect of ozonized oxygen (containing about 5 per cent ozone) at 0° C. on a fraction of Kurokawa petroleum, boiling between 150° and 300° C., and consisting principally of saturated hydrocarbons. After treatment, the oil was mixed with water and heated. It was observed that the iodine value, acid value, specific gravity, refractive index and viscosity were higher but the rotary power was lower than that of the original. The extent to which these changes took place was found to depend upon the length of the period of treatment. With a higher fraction (liquid parmaceutical paraffin) similar results were obtained except that the refractive index and iodine value did not change.

[87a] U. S. Patents 1,918,254 and 1,918,255, July 18, 1933; assigned to V. N. Roadstrum; *Chem. Abs.*, 1933, 27, 4909.

[88] Brus and Peyreshlanques. *Compt. rend.*, 1930. 190. 501.

[89] *Ber.*, 1912, 45, 936; *Chem. Soc. Abs.*, 1912, 102 (1), 407.

[90] British Patent 273,832, 1926; *Brit. Chem. Abs.* B, 1927, 661. Canadian Patent 279,396, 1927; *Chem. Abs.*, 1928, 22, 2755; U. S. Patent 1,689,599, Oct. 30, 1929; *Chem. Abs.*, 1929, 23, 275.

[91] *J. Soc. Chem. Ind. Japan*, 1926. 29. 7; *Chem. Abs.*, 1926, 20. 1512.

On prolonged treatment of lubricating oils with ozone, Dover and Cromwell[92] noted that the coefficient of static friction was reduced with paraffin base oils though a less regular and pronounced change took place with asphaltic base oils. They failed to obtain any definite relationship between the physical and chemical properties of the oil and its value as a lubricant. Unsaturated oils appeared to be more efficient lubricants than more highly saturated oils.

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[92] *Ind. Eng. Chem.*, 1927, 19, 94.

Chapter 37

Oxidation of Methane and Its Homologues

In this chapter the oxidation of saturated hydrocarbons is considered particularly from the standpoint of the production of substances other than aldehydes. Such substances include oxides of carbon, water, hydrogen, and unsaturated hydrocarbons. Several theories of the mechanism of the oxidation of hydrocarbons are also discussed. The methods employed in the preparation of these oxidized substances belong to the slow combustion or non-explosive type. The explosive oxidation of hydrocarbons is considered in Chapter 44. Furthermore, this discussion is limited to the oxidation of the gaseous or relatively low-boiling hydrocarbons. The oxidation of high-boiling liquid and solid hydrocarbons is reviewed in two later chapters (42 and 43) relating to the production of acids and the oxidation of paraffin wax.

OXIDATION OF METHANE

A study of the oxidation mechanism of methane made by Bone and Wheeler[1] showed that, in the presence of an excess of methane, the reaction between methane and oxygen took place at temperatures below the ignition point. In no case was there a preferential oxidation of either element of the hydrocarbon molecule, inasmuch as neither free hydrogen nor free carbon was observed at any stage of the oxidation. In slow-oxidation experiments they isolated formaldehyde as an intermediate oxidation product. This evidence served as a basis for the hydroxylation theory of oxidation. Briefly, this theory states that oxidation proceeds through the successive conversion of the hydrogen atoms (attached to a carbon atom) to hydroxyl groups.[2] Oxidation in the presence of a catalyst was held to take place in exactly the same way, however, with this difference: hydroxylation progressed with such velocity that intermediate oxidation products could not be detected. Only end-products such as the oxides of carbon and water were obtained. Later work by Bone and Drugman[3] with explosive mixtures of hydrocarbon gases indicated that this same explanation, with some slight modification, was also applicable.

Although other theories have been proposed (and these will be discussed later) it is certain that one of the intermediate oxidation products of methane is formaldehyde and from that stage onward the oxidation mechanism is clear. Depending upon the conditions under which oxidation is taking place, the formaldehyde may either yield hydrogen and carbon monoxide by decomposition, or the aldehyde may be oxidized to formic acid. The formic acid, in turn, can be oxidized to carbonic acid, which then yields carbon dioxide and water by decomposition.

Newitt and Haffner[4] isolated another intermediate oxidation product, methyl

[1] *J.C.S.*, 1902, **81**, 535; 1903, **83**, 1074.

[2] A diagrammatic representation of the reactions taking place is given in Chapter 8. See Bone and Townend, "Flame and Combustion in Gases," Longmans, Green and Co., New York, 1927, for further discussion of this subject. Also Bone, *J.C.S.*, 1933, 1599.

[3] *J.C.S.*, 1906, **89**, 674.

[4] *Proc. Roy. Soc.* (*London*), 1932, **A134**, 591; *Brit. Chem. Abs.* **A**, 1932, 232; Newitt and Bloch, *Proc. Roy. Soc.* (*London*), 1933, **A140**, 426; *Brit. Chem. Abs.* **A**, 1933, 678; *Cf.* Bone, *Nature*, 1931, **127**, 481; *Brit. Chem. Abs.* **A**, 1931, 598; Bone and Allum, *Proc. Roy. Soc.* (*London*), 1932, **A134**, 578; *Chem. Abs.*, 1932, **26**, 2697.

alcohol, by the reaction of methane and oxygen at 360° C. under 100 atmospheres pressure. With a 9: 1 mixture of methane and oxygen the reaction was complete in a few minutes. Seventeen per cent of the methane oxidized was recovered as methyl alcohol, 0.6 per cent as formaldehyde, and the remainder as carbon monoxide and dioxide and water. No hydrogen was formed and no evidence of the formation of peroxides was found.

The rate of oxidation of methane in a quartz tube was found to increase exponentially with time and to result finally in ignition of the methane-oxygen mixture. Kovalskii, Sadovnikov and Chirkov,[5] believed the oxidation to be predominantly a surface reaction.

The oxidation of approximately 4 per cent of methane in air in the presence of metals, metallic oxides, and mixtures of oxides has been investigated by Yant and Hawk.[6] The temperatures at which oxidation occurred in their experiments varied from 150° to 350° C. Of the catalysts used, cobaltic oxide was found to be the most efficient, with manganese dioxide and nickel (ic) oxide next in order. Mixtures of oxides gave results corresponding to the proportion of each active material. Metallic nickel and platinum black were the least effective. The addition of 10 per cent of platinum black to metallic nickel appeared to act as a promoter, as the efficiency of the mixture was greater than that of either of the metals alone. Analysis of the gases after oxidation indicated that the products of the reaction were carbon dioxide and water.

With metallized silica gels at temperatures varying from 200° to 400° C. Reyerson and Swearingen[7] observed the complete oxidation of methane by oxygen. Only carbon dioxide resulted, no intermediate oxidation products being obtained. The metals used were silver, copper, palladium and platinum. Silver did not exert any catalytic effect upon the methane oxidation. With copper, oxidation started at 200° C.; with platinum, at 240° C.; and with palladium, at 330° C. Copper had to be oxidized before it was catalytically active. The platinized gel probably adsorbed oxygen better than the palladium gel which might, therefore, account for its greater activity. It was observed that there was a limited range of oxygen content in which maximum oxidation occurred and above and below which the effect of the catalyst decreased. With platinized silica gel and with about 28 per cent oxygen in the gas mixture, nearly 2 per cent of the methane was oxidized to carbon dioxide and water.

Campbell[8] investigated the oxidation of methane with the following catalysts: silver and copper supported on pumice, vanadium oxides on pumice, platinized asbestos, platinum black and palladium black on asbestos. A wide range of temperatures was used, varying from 172° C. to as high as 700° C. No intermediate oxidation products, or only traces, were noted when silver, platinized asbestos and platinum black catalysts were employed. With copper, however, some formaldehyde was produced between the temperatures of 397° and 517° C. This aldehyde was formed also with palladium black below 400° C. and with vanadium oxides on pumice between the temperatures of 520° to 640° C. With two of the catalysts, silver and vanadium oxides, free hydrogen was found in the gases after oxidation.

Although, in the presence of catalysts, the various stages of oxidation or decomposition succeed each other so rapidly that difficulty was experienced by Campbell in attempting to isolate intermediate products in any quantity, nevertheless, the results were considered to be in accord with Bone's hydroxylation theory.

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[5] *Physik. Z. Sowjetunion,* 1932, 1, 451; see also Neumann and Egorov, *ibid.,* 1932, 1, 700; *Chem. Abs.,* 1932, **26**, 5481.

[6] *J.A.C.S.,* 1927, **49**, 1454.

[7] *J. Phys. Chem.,* 1928, **32**, 192; *Chem. Abs.,* 1928, **22**, 1520.

[8] *J.S.C.I.,* 1929, **48**, 93T.

The course of oxidation, however, varied with the catalysts and the temperature. Thus, after the aldehyde stage has been reached, vanadium oxides apparently favor the decomposition of the aldehyde to hydrogen and carbon monoxide, with the subsequent oxidation of these latter products to water and carbon dioxide. Palladium black, on the other hand, seems to favor the oxidation of the aldehyde to formic acid, followed by thermal decomposition to water and carbon monoxide, and subsequent oxidation of the carbon monoxide to dioxide.

The conditions under which methane in contact with copper oxide undergoes complete combustion to water and carbon dioxide have received considerable attention. Though this is of particular interest in analysis of this compound, some of the conclusions are pertinent to oxidation in general.

Campbell and Gray[9] studied the combustion of methane, methane-hydrogen, and methane-ethylene mixtures by copper oxide, lead chromate and cobalt oxide. They showed that below 280° C. the proportion of carbon dioxide formed with copper oxide is practically negligible at moderate periods of contact. Up to 400° C. oxidation is slow but at 700° C. the rate is very rapid and complete combustion is effected within 7 minutes. The addition of cuprous chloride, cobalt oxide, manganese dioxide, nickel oxide and vanadium pentoxide to copper oxide promotes the oxidation. If hydrogen or ethylene is added to methane the temperature required for complete oxidation is reduced. Fused lead chromate is inferior to and cobalt oxide is no better than copper oxide for this oxidation. Wheeler[10] investigated the kinetics of the combustion of methane by copper oxide and tentatively suggested that the reaction took place at the copper-copper oxide interface. The study was extended to ethane, propane, butane, hydrogen, and carbon monoxide by King and Edgecombe.[11] It was found that at 280° C. with a 10-minute contact period, copper oxide effected the oxidation of no methane, 0.8 volume per cent ethane, 1.0 volume per cent propane and 1.4 volume per cent butane. These rates increased with a rise in temperature.

A further investigation of the oxidation of methane by metallic oxides brought out the following facts:[12] Copper oxide and methane begin to react at 350° C., and at 725° C. water and carbon dioxide are formed quantitatively. Ferric oxide (Fe_2O_3) is completely reduced to Fe_3O_4 at 680° C., carbon dioxide and water being formed. Zinc oxide begins to react at 800° C., but even at 1000° C. only 50 per cent oxidation occurs. The products in this case are carbon monoxide and hydrogen with traces of carbon. Stannic oxide is unreactive below 800° C. but at 972° C. it effects 73 per cent oxidation to carbon dioxide and water.

Yoshikawa[13] oxidized methane with air under ordinary pressure at 600° C., the products being carbon monoxide and dioxide, formaldehyde, methyl alcohol and formic acid. The same substances were formed by oxidation at 300° to 400° C. at pressures from 12 to 100 atmospheres.[14] Increase of pressure brought about greater yields of methyl alcohol. Hydrogen appears at higher temperatures (700 ° C. under 1 atmosphere pressure). The results indicated a chain reaction mechanism, for on enlarging the reaction vessel oxidation was suppressed and the proportions of methyl alcohol and formaldehyde were greater. Addition of nitric acid promoted the reaction but lead tetraethyl had a retarding influence.

[9] *J.S.C.I.*, 1930, **49**, 432T; *ibid.*, 1930, **49**, 447T; *ibid.*, 1930, **49**, 450T. These papers include a bibliography of the subject.

[10] *Rec. trav. chim.*, 1931, **50**, 874; *Chem. Abs.*, 1931, **25**, 5339.

[11] *Dept. Sci. Ind. Res., Fuel Res., Tech Paper* **33**, 1931; *Brit. Chem. Abs.* **B**, 1932, 215.

[12] Neumann and Wang, *Angew. Chem.*, 1933, **46**, 57; *Brit. Chem. Abs.* **B**, 1933, 257.

[13] *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1931, **10** (3), 251; *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1931, **15**, 289-291, Abstract 30-31; *Chem. Abs.*, 1931, **25**, 2411.

[14] Yoshikawa, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1931, **10**, 305; *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1931, 15, 294-296. Abstract 35-36; *Chem. Abs.*, 1931, **25**, 4842.

The oxidation of methane to carbon monoxide and hydrogen was also studied.[15] The most efficient catalyst for this reaction is nickel, together with silica or thoria as promoters. At 850° to 900° C. methane and oxygen react almost quantitatively to yield carbon monoxide and hydrogen. The production of hydrogen from methane by oxidation with air or oxygen has been the subject of considerable research.[16] In one such process [17] the catalysts are metallic oxides capable of being reduced to lower oxides, for example, titanium dioxide or a mixture of chromium and magnesium oxides. The production of hydrogen by oxidation of hydrocarbons with steam has already been reviewed in Chapter 10.

The oxidation of methane by zinc oxide has been suggested by Doerner [18] as a method for the refining of zinc. At about 927° C., zinc oxide and methane react to yield zinc (vapor), carbon monoxide and hydrogen, according to the following:

$$ZnO + CH_4 \longrightarrow Zn\,(gas) + CO + 2H_2$$

The temperatures in this process are kept below 1000° C. Although the reaction rate increases with higher temperatures, the formation of carbon dioxide and subsequent reoxidation of the zinc also increase. Crude natural gas gives practically the same results as methane, the greater reducing power of the homologues of methane being compensated for by their greater tendency towards thermal decomposition. This method was suggested by de Simó [18a] for the production of carbon monoxide and hydrogen.

Oxidation takes place on passing a stream of methane, or gases rich in methane, into heated concentrated sulphuric acid which contains a very small quantity of mercury.[18b] At 180° C. the evolution of sulphur dioxide begins and the methane content of the exit gases decreases while the carbon dioxide content increases. The main reaction appears to be the oxidation of methane to carbon dioxide, the sulphuric acid being reduced to sulphur dioxide and water.

$$CH_4 + 4H_2SO_4 \longrightarrow CO_2 + 6H_2O + 4SO_2$$

Brewer and Kueck [19] observed that methane is quantitatively converted into ethylene and hydrogen in the glow discharge at the temperature of liquid air, one molecule of ethylene being formed per CH_4^+ ion. When oxygen is mixed with the methane the products are carbon dioxide and water. The reaction seems to be initiated primarily by the CH_4^+ ions, and is accelerated by excess methane and retarded by excess oxygen. The maximum rate occurs with a mixture of equal volumes of methane and oxygen. The oxidation is most pronounced in the negative glow, is negligible in the dark spaces, and is approximately constant throughout the positive column. The efficiency of the positive column (in terms of electron volts per molecule) rapidly increases with pressures above 5.5 mm., indicating the presence of ionic chain reactions.

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[15] Yoshikawa, *Bull. Chem. Soc. Japan,* 1931, **6**, 106; *Brit. Chem. Abs.* **A**, 1931, 693.

[16] Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930, 771; see, Marek and Hahn, "The Catalytic Oxidation of Organic Compounds in the Vapor Phase," Chemical Catalog Co., Inc., 1932, 260; Keller and Klempt, *Ber. Ges. Kohlentech.,* 1930, **3**, 230; *Brit. Chem. Abs.* **B**, 1931, 325; Burke, U. S. Patent 1,843,063, Jan. 26, 1932; assigned to Combustion Utilities Corp., *Chem. Abs.,* 1932, **26**, 1727; B.A.S.-F., British Patent 231,218, 1923; *J.S.C.I.,* 1925, **44**, 357B; British Patent 266,410, 1925; *Brit. Chem. Abs.* **B**, 1927, 316. See also Taylor and Russell, *Gas Age Record,* 1933, **71**, 333; *Chem. Abs.,* 1933, **27**, 3317.

[17] Wilke and Fried, German Patent 525,556, 1929; *Chem. Abs.,* 1931, **25**, 4672; French Patent 701,003, 1930; *Chem. Abs.,* 1931, **25**, 3780; both patents assigned to I. G. Farbenindustrie A.-G.

[18] Doerner, *Bur. Mines, Rept. Investigations* 3091; *Chem. Abs.,* 1931, **25**, 2674.

[18a] British Patent 373,701, 1930; *Chem. Abs.,* 1933, **27**, 2563; Canadian Patent 319,121, 1932; *Chem. Abs.,* 1932, **26**, 2023; Dutch Patent 29,302, 1933; *Chem. Abs.,* 1933, **27**, 3299; patents assigned to Bataafsche Petroleum Maatschappij; U. S. Patent 1,899,184, Feb. 28, 1933; assigned to Shell Development Co.; *Chem. Abs.,* 1933, **27**, 3063.

[18b] Fischer and Bahr, *Ges. Abhandl. Kenntnis Kohle,* 1924, **8**, 281; *Chem. Abs.,* 1930, **24**, 5282.

[19] *J. Phys. Chem.,* 1931, **35**, 1293; *Brit. Chem. Abs.* **A**, 1931, 919.

The effect of inert gases on the oxidation of methane has been studied by Melville,[20] who found that the velocity of oxidation is governed by a factor which is inversely proportional to the diffusion coefficient of the reaction chains through the gas mixture.

OXIDATION OF ETHANE

From work on the slow-combustion of ethane at temperatures of 300° to 500° C., Bone[21] concluded that the reaction proceeded in a manner similar to that for methane. Ethane, however, under analogous conditions burned more rapidly than methane. In the presence of insufficient oxygen for complete combustion there was no preferential oxidation of either carbon or hydrogen. On the other hand, oxidation appeared to proceed in stages, with the formation of aldehydes, water, carbon monoxide and dioxide. All the steps were in accord with the Bone hydroxylation theory. The appearance of hydrogen or methane, or both, among the products of the reaction and the absence of any liberated carbon was attributed to the thermal decomposition of the aldehydes formed: formaldehyde yielding a mixture of hydrogen and carbon monoxide, and acetaldehyde yielding methane and carbon monoxide. Ethylene was also found, probably as the result of thermal decomposition of ethane. The oxidation of ethane, therefore, appears to be a much more complicated reaction than that of methane. Later, Bone and his collaborators[22] showed that the oxidation reactions which took place in the explosive combustion of hydrocarbons were similar to those in the non-explosive or slow-combustion of such substances.

In a further study[23] of the slow-combustion of ethane efforts were made to determine if peroxides were formed at any stage. The investigation was conducted over a temperature range of 290° to 323° C. and at initial pressures of 440 to 778 mm. The results indicated that oxidation proceeds homogeneously throughout the medium, though it may be greatly retarded by increasing the surface exposed to the gases. It was preceded, however, by a well-defined induction period, which could be shortened or obliterated by the addition of small quantities of ethyl alcohol, formaldehyde, iodine or nitrogen peroxide, without altering the non-explosive character of the reaction. The addition of 1 per cent of acetaldehyde vapor results in the instantaneous inflammation of the mixture. A rise in temperature as well as an increase in pressure also shortens the induction period. These same factors affect the reaction period in a similar manner. Both the induction and reaction periods are much shorter for a gaseous mixture consisting of two molecules of ethane and one of oxygen than for a mixture of the gases in equimolecular proportion. An increase of the oxygen content beyond this latter proportion still further increases both of these periods. This experimental demonstration is in agreement with the hydroxylation theory and is not what might be expected according to the peroxide theory of combustion. Although small quantities of peroxides may be formed at the aldehyde stage no evidence was obtained of an earlier peroxide formation. Indirect indications showed that either ethyl alcohol or some lower "oxyethane" was the initial product in the combustion of ethane.

Taylor and Riblett[24] investigated the progress of oxidation of ethane by observing the rate of change of pressures for mixtures of ethane and oxygen at different temperatures. In all experiments a short induction period of about 2 minutes was noted, followed by a slow reaction which was accelerated in the same manner as autocatalytic reactions. The oxidation exhibited all the characteristics of a chain reaction,[25] namely: (1) great sensitiveness to foreign substances, (2) negative surface effect (effect of increased surface in the reaction chamber), (3) specific effect of diluent gases, and (4) an induction period.

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[20] *Trans. Faraday Soc.*, 1932, **28**, 814; *Chem. Abs.*, 1933, **27**, 461; effect of inert gases on oxidation of hydrogen sulphide, carbon disulphide, hydrogen, phosphine and phosphorus is also reported.

[21] Bone and Stockings, *J.C.S.*, 1904, **85**, 693.

[22] Bone, Drugman and Andrew, *J.C.S.*, 1906, **89**, 1614; Bone and Drugman, *J.C.S.*, 1906, **89**, 660.

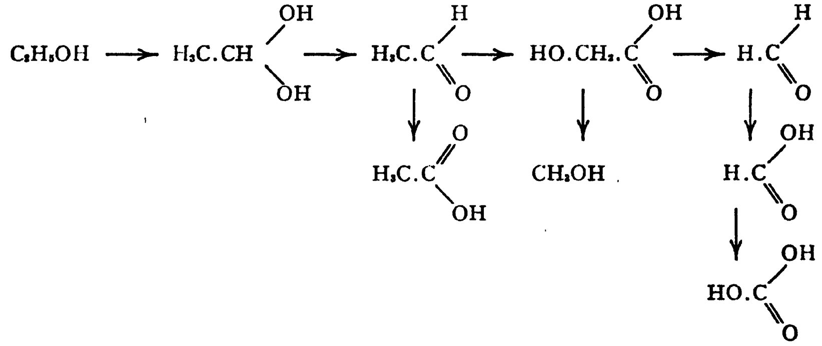
[23] Bone and Hill, *Proc. Roy. Soc.*, 1930, **A129**, 434; *Brit. Chem. Abs.* **A**, 1931, 45.

[24] *J. Phys. Chem.*, 1931, **35**, 2667; *Chem. Abs.*, 1931, **25**, 5827.

It was also observed that with the oxygen in excess the rate of reaction was directly proportional to the oxygen pressure. Increasing the proportion of ethane while keeping the oxygen constant accelerated the reaction so greatly that it was difficult to avoid explosions.

Considering the oxidation of ethane as a chain reaction,[26] Taylor and Riblett calculated the energy of activation for a 1:3.5 mixture of ethane and oxygen as 43,000 calories at 200 mm. pressure, 38,000 calories at 215 mm., and 32,000 calories at 300 mm. These values indicated that the reaction chains were not very long.

Newitt and Bloch[27] used pressures of 15 to 100 atmospheres and temperatures of 260°-316° C. in their study of the slow combustion of ethane-oxygen mixtures containing from 85 to 90 per cent ethane. The products consisted of water, methyl alcohol, formaldehyde, formic acid, and acetaldehyde with a predominant proportion of ethyl alcohol and acetic acid. Increased pressure favored the survival of substances which result without rupture of the ethane molecule. Representatives of each step postulated in the hydroxylation theory were isolated:



No peroxides were found, hence the hydroxylation theory of oxidation was favored.

In ethane-oxygen mixtures held at a given temperature, the pressure first increases exponentially with time, passes through a maximum and then decreases. If the initial pressure is below a definite limiting value an explosion results when the pressure maximum is reached. Kovalskii, Sadovnikov, and Chirkov [27a] observed this in their study of the oxidation rate. The surface of the reaction vessel was probably activated in the course of a run, for washing it with sodium chloride solution greatly reduced the initial pressure rise, but treatment with hydrogen fluoride, on the other hand, accelerated it.

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[25] The critical explosion pressures agree with those of thermal explosion predicted by Semenoff's theory of reaction velocity (*Z. physik. Chem.*, Abt. B, 1929, 2, 161; *Chem. Abs.*, 1929, **23**, 2870), but Taylor and Riblett consider the reaction best explained as chain explosions preceded by thermal accelerations.

[26] Other explanations of oxidation by a series of chain reactions have been proposed. See, for example, Kistiakowsky and Lenher, *J.A.C.S.*, 1930, **52**, 3785, and Spence and Kistiakowsky, *J.A.C.S.*, 1930, **52**, 4837, for oxidation of acetylene; Bodenstein, *Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1931, III; *Z. physik. Chem.*, 1931, **B12**, 151; *Brit. Chem. Abs.* **B**, 1931, 572, for oxidation of acetaldehyde and hydrocarbons; Bäckström, *J.A.C.S.*, 1927, **49**, 1460; *Med. K. Vetenskapsakad. Nobelinst.*, 1927, 6, No. 15 and 16; *Brit. Chem. Abs.* **A**, 1927, 1151, for autoxidation of benzaldehyde, heptaldehyde, and sodium sulphite.

[27] *Proc. Roy. Soc. (London)*, 1933, **A140**, 426; *Chem. Abs.*, 1933, **27**, 3443.

OXIDATION OF HIGHER PARAFFIN HYDROCARBONS

The non-explosive oxidation of propane and of n- and iso-butanes has been investigated by Pease.[28] Mixtures of propane and oxygen were passed through glass tubes heated at 300° to 625° C. No attempt was made to analyze the liquid products of the reaction and all conclusions, therefore, were based on gas analyses. The reactions taking place were classified into three types which, using propane as an example, are as follows:

(1) Dissociation: $C_3H_8 \longrightarrow C_3H_6 + H_2$

(2) Unsaturation by Oxidation: $C_3H_8 + \frac{1}{2}O_2 \longrightarrow C_3H_6 + H_2O$

(3) Aldehyde Formation: $C_3H_8 + 2O_2 \longrightarrow CO + 2H_2O + CH_3CHO$

The dissociation (Reaction 1) and the unsaturation by oxidation (Reaction 2) of propane are homogeneous gas reactions of the first order and appear at 500°-600° C. They are subject, however, to induction by the aldehyde formation reaction (3) at lower temperatures. Aldehyde formation appears to be a chain reaction of the luminous type and begins at 300°-350° C. It is particularly sensitive to suppression by minor changes such as an increase in the area of the surfaces of contact, reduction of the pressure, or dilution of the gas mixture with gases such as oxygen, methane, or nitrogen. Suppression by dilution with gases is greater at higher temperatures, so that the reaction may have a negative temperature coefficient, even though it eventually becomes explosive.[29] Low temperatures favor the production of aldehydes containing one carbon atom less than the original hydrocarbon. High temperatures and maximum suppression favor the formation of olefins.

Both n- and iso-butane react similarly to propane, but they are more readily oxidized. Of the two butanes, n-butane is the more reactive.

The partial oxidation of pentane by air in the presence of a platinum catalyst supported on asbestos [30] resulted in the formation of water, formaldehyde, and amylene as condensible products and carbon dioxide, ethylene, propylene, butylene, amylene and butadiene as gaseous products. When hexane was substituted for pentane a considerable proportion of hexylene was obtained. In oxidation reactions of this type, polymerized materials are always found with the unsaturated hydrocarbons.

Mixtures of equal volumes of pentane and oxygen showed an induction period followed by an increase in rate of pressure rise when heated in glass at 245° C. and 760 mm. According to Pidgeon and Egerton,[31] rapid heating, change of concentration, or lowering of pressure raises the temperature required for reaction, and dilution with nitrogen or use of silica vessels lowers it. Naphthalene was formed by incomplete combustion of normal pentane, but not of normal hexane, heptane, or octane, as shown by Mondain-Monval and Quanquin.[32]

[27a] *Physik. Z. Sowjetunion*, 1932, 1, 451; see also Neumann and Egorov, *ibid.*, 1932, 1, 700; *Chem. Abs.*, 1932, 26, 5481.

[28] *J.A.C.S.*, 1929, 51, 1839; *Brit. Chem. Abs.* A, 1929, 905.

[29] *Cf.* Bone, Stockings and Wheeler, *J.C.S.*, 1904, 85, 693, 1637.

[30] Stepski, *Monatsh.*, 1902, 23, 773; also, Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 515.

[31] *J.C.S.*, 1932, 661.

From their work with hexane Brunner and Rideal[33] concluded that the oxidation of hydrocarbons was very similar to the autoxidation of benzaldehyde. There is a period of induction during which peroxide molecules are formed and react with hexane molecules. This induction period is greatly shortened by increased oxygen pressure. Aniline exerts an inhibiting effect on the oxidation, and surface catalysts such as pumice cause slow combustion accompanied by slight decreases of pressure. The temperature of initial combustion, furthermore, is not a characteristic of the hydrocarbon, for rapid combustion will set in after a period of induction at lower temperatures.

When a mixture of hexane and oxygen (42 per cent hexane, 57 per cent oxygen and 1 per cent nitrogen) is heated in a closed vessel there is always a period of induction during which the pressure increases very slowly, followed by a rapid increase of pressure.[34] This period of increased pressure is associated with an oxidation by the peroxide molecules formed during the induction period, and includes reactions which result in the formation of water, unsaturated compounds, fatty acids, carbon monoxide and dioxide and other gases. The unsaturated intermediate products thus formed take up oxygen and form new (secondary) peroxides. The decomposition and reaction of both primary and secondary peroxides results in a series of further changes which lead to the production of aldehydes, peracids and other products. Soon after the peroxide formation has attained a maximum value all of the free oxygen disappears. A further production of peroxides, moloxides, water and fatty acids, therefore, cannot occur even though the decomposition of the peroxides present into carbon monoxide and dioxide and other gases continues. It is this decomposition which causes a marked increase in the pressure toward the end of the reaction.

It has also been shown that the absorption of oxygen during the induction period is very rapid. The reactions may be represented as follows:[35]

$$
\begin{aligned}
&C_6H_{14} + O_2 \longrightarrow C_6H_{14}\dot{O}_2 \text{ (active moloxide)}\\
&C_6H_{14}O_2 + C_6H_{14} \longrightarrow H_2O + 2C_6H_{12}\\
&C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition}
\end{aligned}
$$

Time-pressure curves were constructed from the oxidation of various saturated cyclic hydrocarbons having side chains.[36] Temperatures between 200° and 700° C. and an initial pressure of 1110 millimeters were chosen. In every case, the pressure remained constant for a considerable time, then fell and passed through a minimum, followed by a steady rise. Ultimately it tended to become constant. 1,1-Dimethylcyclohexane varied from the others in that no minimum was observed. The apparent induction period became shorter as the length of the side chain increased, indicating that impurities were not the sole influence on the rate of oxidation. The conclusions reached as to the meaning of the minimum point is that oxidation takes place according to the peroxide theory, peroxides being formed at this minimum and initiating the reaction chains.

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[32] *Ann. chim.*, 1931, (10) **15**, 309; *Chem. Abs.*, 1931, **25**, 5548.

[33] *J.C.S.*, 1928, **130**, 1162, 2824; also, Brunner, *Helv. Chim. Acta*, 1928, **11**, 881; *Chem. Abs.*, 1929, **23**, 323.

[34] See also Pidgeon and Egerton, *J.C.S.*, 1932, 676.

[35] *Cf.* Schläpfer and Brunner, *Schweiz. Ver. Gas u. Wasserfach Monatsh. Bull.*, 1929, **9**, 161; *Chem. Abs.*, 1929, **23**, 4549.

[36] Lewin, *Bull. soc. chim. Belg.*, 1933, **42**, 141; *Brit. Chem. Abs.* **A**, 1933, 786.

This theory of the formation of an active moloxide,[37] which is subsequently converted into a more stable peroxide which then reacts in either the gas phase or on surfaces when its concentration reaches a critical value, differs greatly from the hydroxylation theory proposed by Bone.

Hexane, cyclohexane, and cyclohexene absorb oxygen readily when heated. When mixtures in the proportions of 1 molecule of oxygen to 4 molecules of these hydrocarbons were passed through a furnace, Estradère[38] observed that the formation of peroxides reached a maximum at 330°, 340°, and 410° C., respectively, carbon monoxide appearing simultaneously. Peroxides disappear at high temperatures. Accordingly, cyclicization of saturated hydrocarbons increases their resistance to oxidation only slightly but unsaturation gives marked effects.

The production of peroxides during the direct oxidation of hydrocarbons with air was also observed by Mondain-Monval and Quanquin.[39] On oxidizing pentane, hexane, octane, or gasoline in the vapor state at 300° C., or at slightly lower temperatures, with air there was obtained, in addition to the gaseous products, an oily liquid which possessed marked oxidizing properties. This liquid, on treatment with sodium hydroxide, yielded hydrogen, methyl alcohol, and sodium formate. When heated to 200° C. it underwent an exothermic change with the production of a blue luminescence and white fumes. Simultaneously, large quantities of aldehydes, particularly formaldehyde, were formed. This oily liquid was considered to be a mixture of peroxides, including methyl and ethyl peroxides. The inflammation of mixtures of hydrocarbons and air at relatively low temperatures is attributed[40] to the explosive decomposition of the peroxides. The production of a luminescence during the oxidation of hydrocarbons was noted by Brunner and Rideal,[41] Prettre, Dumanois and Laffitte,[42] and also by Pope, Dykstra and Edgar.[43] The latter workers investigated the non-catalytic oxidation of n-octane and five other isomeric octanes.

In the vapor phase oxidation of n-octane it was found that the gaseous products were carbon monoxide, carbon dioxide, and a small quantity of an unidentified gas which was absorbed by fuming sulphuric acid. Neither hydrogen nor methane could be detected among these gases. The condensible products consisted of unoxidized octane, aldehydes, peroxides and water. Below 200° C. practically no oxidation takes place. Between 200° C. and 270° C. there is an appreciable oxygen consumption though the amount of gaseous products is very small. Practically no carbon monoxide is detected until the temperature is about 270° C. The quantity of carbon dioxide formed, however, increases regularly from zero at 200° C. to 0.4 mole per mole of octane fed to the reaction chamber at 270° C. Above 270° C. the quantity of carbon monoxide produced increases very rapidly, reaching a maximum at 650° C.; at this temperature the ratio of carbon monoxide to carbon dioxide is nearly 3.5:1. The quantity of carbon dioxide formed during this same period (270° to 650° C.) increases very slowly, reaching a maximum value at 400° C., and remaining constant above this temperature. Above 650° C. the carbon monoxide content of the gaseous products decreases very rapidly with increasing temperature and becomes practically zero at 670° C. The carbon dioxide content, on the other hand, increases very rapidly until it becomes practically the only gaseous product. The oxidation of octane is luminescent above 270° C. and the intensity of the luminescence increases with rising temperatures.

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[37] This concept of the formation of moloxides, or peroxides, goes back further. For earlier explanations of oxidation phenomena based on this theory see Engler and Wild, *Ber.*, 1897, **30**, 1669; Bach, *Compt. rend.*, 1897, **124**, 951; Grün, Ulbrich and Wirth, *Ber.*, 1920, **53**, 987.

[38] *Compt. rend.*, 1933, **196**, 674; *Chem. Abs.*, 1933, **27**, 2940.

[39] *Compt. rend.*, 1930, **191**, 299; *Brit. Chem. Abs.* **A**, 1930, 1157.

[40] Mondain-Monval and Quanquin, *Ann. chim.*, 1931, (10) **15**, 309; *Chem. Abs.*, 1931, **25**, 5548.

[41] *Loc. cit.*

[42] *Compt. rend.*, 1930, **191**, 329, 414; *Chem. Abs.*, 1930, **24**, 5498, 5994.

[43] *J.A.C.S.*, 1929, **51**, 1875, 2203.

The data seem to indicate that the first step in the oxidation of n-octane is the formation of the aldehyde:

$$CH_3(CH_2)_6CH_3 + O_2 \longrightarrow CH_3(CH_2)_6CHO + H_2O$$

Octaldehyde is then oxidized to heptaldehyde accompanied by the liberation of carbon monoxide or dioxide, as follows:

Main Reaction, $CH_3(CH_2)_6CHO + O_2 \longrightarrow CH_3(CH_2)_5CHO + HO_2 + CO$
Side Reaction, $CH_3(CH_2)_6CHO + 1\frac{1}{2}O_2 \longrightarrow CH_3(CH_2)_5CHO + HO_2 + CO_2$

Oxidation then continues in similar steps, the product each time being an aldehyde containing one carbon atom less than the substance being oxidized.

At temperatures above 650° C. oxidation of n-octane to carbon dioxide and water was found to take place so rapidly that it was practically explosive. The luminescence associated with carbon monoxide formation at the lower temperatures was still seen. This indicated that the oxidation of aldehydes to lower aldehydes, carbon monoxide and water also takes place at the higher temperatures. The luminescence observed during both low and high temperature oxidation, also probably indicates the occurrence of chain reactions.

Other octanes studied by Pope, Dykstra and Edgar were: 3-methylheptane, 2-ethylhexane, 2,5-dimethylhexane, 2-methyl-3-ethylpentane, and 2,2,4-trimethylpentane. From the data obtained it appeared that the oxidation of the first four isomeric octanes proceeded in a manner similar to that of n-octane, that is, the primary product was an aldehyde which could be further oxidized to yield either a lower aldehyde, carbon monoxide and water, or a lower aldehyde, carbon dioxide and water. These reactions progress until products are formed which resist further oxidation, or until temperatures are reached which are high enough to bring about complete oxidation with the formation of carbon dioxide and water. In general, the methyl group at the end of the longest open-end straight chain is attacked by the oxygen, yielding an aldehyde and water. This aldehyde is then oxidized forming another aldehyde of one less carbon atom, water, and either carbon monoxide or dioxide. The reaction proceeds in this manner until a fork in the hydrocarbon chain is reached when the oxidation product will be a ketone instead of an aldehyde. At this point oxidation becomes slower, as ketones are much more resistant to oxidation than aldehydes.

The temperatures at which oxidation begins vary with the different octanes. With 3-methylheptane and 2,5-dimethylhexane these investigators found that it began at a temperature slightly above 200° C.; with 3-ethylhexane at 250° C.; and 2-methyl-3-ethylpentane, at nearly 300° C. Apparently the more condensed the structure of the hydrocarbon the higher the temperature required. The highly condensed structure of 2,2,4-trimethylpentane rendered the hydrocarbon so resistant that no reaction occurred until such high temperatures were reached that complete oxidation took place very rapidly.

Chavanne and Tock[44] found that the induction period decreased with increasing molecular weight. This was shown by the slow oxidation of octane, nonane and decane. A mixture of the hydrocarbon and oxygen was heated to 120° C. The gaseous products were the same in each case, viz.: from 30 to 40 per cent carbon dioxide, 1 to 3 per cent carbon monoxide, 5 to 7 per cent hydrogen, and 1 to 2 per cent paraffins. The liquid fractions consisted of formic, acetic, and succinic acids, and formaldehyde. In addition, the liquid portions from decane contained methyl octyl ketone, that from nonane, methyl heptyl ketone, and from octane, octanol and methyl hexyl ketone. In all cases acids were formed containing 1 carbon atom less than the original hydrocarbon. These acids were incompletely identified. The presence of preponderant proportions of methyl ketones with an equal number of carbon atoms as the original material led to the conclusion that slow-oxidation is not to be regarded as an attack of the terminal carbon atom of the chain.

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[44] *Bull. soc. chim. Belg.*, 1932, **41**, 630; *Chem. Abs.*, 1933, **27**, 2131.

The catalytic vapor-phase oxidation of two tetraalkylmethanes, 3,3-dimethylpentane and 3,3-diethylpentane, studied by Faith, Swann, and Keyes,[45] yielded only water, carbon oxides, unsaturated hydrocarbons and traces of lower aldehydes. In this respect they resemble normal saturated hydrocarbons. The catalysts used were copper, vanadium oxide, and cerium oxide.

The action of oxygen on alkylbenzenes at 100° C. has been investigated by Stephens.[46] The oxidation of methylbenzene was found to proceed in two stages: (1) the formation of the aldehyde, and (2) the oxidation of the aldehyde to an acid. When the side-chain contained more than one carbon atom a ketone was produced, for example, ethylbenzene yielded acetophenone. With compounds having a secondary group as the side-chain, a ketone and an acid were formed. Thus, cumene (isopropylbenzene) was oxidized to acetophenone and formic acid. No oxidation took place with ter.-butylbenzene. Stephens concluded, therefore, that the oxidation of substituted benzenes took place at the α-carbon atom if at least one hydrogen atom was directly attached to it.

The presence of water inhibited the oxidation of the alkylbenzenes when two or three hydrogen atoms were attached to the α-carbon atom, but favored the reaction when only one hydrogen atom was attached. This suggested that in the oxidation of the first two types of compounds there was a reversible stage in which water was eliminated.

Ethylbenzene in liquid phase oxidation is oxidized to acetophenone more rapidly in the presence of manganese acetate than in that of acetic anhydride,[47] according to King, Swann and Keyes.[48] Metallic oxides and acetates of other metals have negligible catalytic action.

Slow-oxidation of liquid 1,3-dimethylcyclopentane[49] at 80° C. yields acetic acid, the methyl isoamyl ketone, $H_3CCOCH_2CH(CH_3)C_2H_5$ and the acid $H_3CCOCH_2CH(CH_3)CH_2COOH$ in the largest proportions. Other products are carbon dioxide, carbon monoxide, hydrogen, traces of methane and ethane, formic acid, small quantities of isopropylacetic and methylethylacetic acids, traces of a hexanoic acid, 1,3-dimethyl-1-cyclopentanol, methyl isobutyl ketone, 1,3-dimethyl-1,3-cyclopentanediol and two ketols, $C_7H_{14}O_2$. Similarly[50] 1,3-dimethylcyclohexane in oxygen at 100° C. under the influence of sunlight gave, as the predominant products, 1,3-dimethylcyclohexanol and a keto-acid which may be either $CH_3COCH_2CH(CH_3)CH_2CH_2COOH$ or $CH_3COCH_2CH_2CH_2CH(CH_3)COOH$ and acetic acid, together with smaller proportions of carbon dioxide and monoxide, hydrogen, methane, possibly propane, formic and acetic acids, two hexanoic acids not fully identified, 6-methyl-2-heptanone, 1,3-dimethyl-1,3-cyclohexanediol. Chavanne and his co-workers thus show the oxidation to be chiefly a hydroxylation of the tertiary carbon atoms, supporting the combustion theory of Bone.

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[45] *Ind. Eng. Chem.*, 1933, **25**, 224.

[46] *J.A.C.S.*, 1926, **48**, 1824, 2920.

[47] *Cf.* Stephens, *loc. cit.*

[48] *Ind. Eng. Chem.*, 1929, **21**, 1227.

[49] Chavanne and Miller, *Bull. soc. chim. Belg.*, 1931, **40**, 611; *Chem. Abs.*, 1932, **26**, 2435.

[50] Chavanne, Pahlavouni and Katzenstein, *Bull. soc. chim. Belg.*, 1931, **40**, 626; *Chem. Abs.*, 1932, **26**, 2435.

The formation of alcohols and aldehydes during the oxidation of paraffin wax was considered by Landa[51] as a clear indication of the correctness of Bone's hydroxylation theory of oxidation, particularly for the slow-combustion of hydrocarbons. A paraffin wax, melting at 51° C., was heated to 280°-300° C. and oxidized by blowing a stream of air through it. The products of the reaction were carried over by the gas and collected in receivers containing water. A portion of these products was soluble in water, but the remainder separated as an oily insoluble layer. Some gases were also obtained, as well as a small quantity of residual asphaltic material. The water-soluble products, after two rectifications, were divided into three fractions with the following boiling ranges: (1) 45°-60° C., (2) 60°-70° C., and (3) 70°-80° C. The aldehydes in each fraction were then converted to acids with silver oxide. These acids were identified by their salts, particularly those of lead and silver. Substances which did not react with silver oxide were also determined. The results thus obtained indicated that the first fraction contained propionic aldehyde and acetone; the second fraction, methyl alcohol and acetone; and the third fraction, ethyl alcohol, methyl ethyl ketone, and butyric aldehyde. In the supernatant oil layer the following aldehydes were identified: oenanthylic, caprylic, nonanylic, capric and undecanylic. The oily layer also contained other substances which were not identified but appeared to be alcohols and higher aldehydes.

Landa and Pokorny[52] identified formaldehyde, acetaldehyde, propionaldehyde, methyl alcohol and acetone in the products of the slow-combustion of 2-methyltricosane, $H_3C(CH_2)_{20}CH(CH_3)CH_3$. The acetone originated from the rupture of the side chain, but since only about 3 per cent of the theoretical yield was obtained, it did not appear to them to be a normal product of combustion. Accordingly, they believe the acetone formed in the slow-combustion of natural paraffins indicates the presence of more highly branched-chain hydrocarbons.[53]

THEORIES OF THE OXIDATION MECHANISM OF SATURATED HYDROCARBONS

Some of the theories which have been advanced to explain the mechanism of the oxidation of saturated hydrocarbons will be summarized briefly.[54] One of the earliest regarded the hydrogen of the hydrocarbon as being preferentially oxidized. This, however, was vigorously opposed by Kersten,[55] who, taking the opposite view, stated that the carbon was burned preferentially either by direct oxidation of the hydrocarbon to form carbon monoxide and hydrogen or by oxidation of the carbon after thermal dissociation of the molecule. This latter view was also held by Misteli.[56]

From the experimental results obtained by Bone and his collaborators[57] on the oxidation of methane, ethane, ethylene, acetylene and other gaseous hydrocarbons, was formulated the hydroxylation theory.[58] This theory postulates the successive oxidation of hydrogen atoms in the hydrocarbon molecule to hydroxyl groups. The resulting compounds then either lose a molecule of water, or break down in one or more ways. For example, methane would be oxidized first to methyl alcohol, and then to methylene glycol, which in turn would decompose to formaldehyde and water. The formaldehyde would then react in one of two ways depending upon the conditions, principally on the temperature under which oxidation was taking place: (1) decompose to yield hydrogen and carbon monoxide, which in turn would be oxidized to water and carbon dioxide, respectively; or (2) be oxidized to formic acid and then to carbonic acid, the latter yielding carbon dioxide and water. This may be represented in the following way:

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[51] *Bull. soc. chim.*, 1928, (4) 43, 529. Also, *Compt. rend.*, 1928, 186, 589; *Chem. Abs.*, 1928, 22, 1948. The oxidation of paraffin wax is discussed in detail in Chapter 43.

[52] *Coll. Czechoslov. Chem. Communications*, 1932, 4, 456; *Chem. Listy*, 1932, 26 (20), 512; *Chem. Abs.*, 1933, 27, 489.

[53] *Cf.* Landa, *Paliva a topeni*, 1929, 11, 1; *Brit. Chem. Abs.* A, 1930, 190.

[54] A rather extensive discussion of such theories, together with an excellent bibliography has been given by Egloff, Schaad and Lowry, *Ind. Eng. Chem.*, 1929, 21, 785. See also Bone, *J.S.C.I.*, 1933, 52, 202T; *J.C.S.*, 1933, 1599.

[55] *J. pr. Chem.*, 1861, 84, 310.

[56] *J. Gasbel.*, 1905, 48, 802; *Chem. Soc. Abs.*, 1905, 88 (1), 849.

[57] *J.C.S.*, 1902, 81, 536; 1903, 83, 1074; 1904, 85, 693, 1637; 1905, 87, 1232; 1906, 89, 660.

[58] An outline of fundamental combustion reactions of natural gas is given by Hoff, *Western Gas*, 1933, 9 (6), 9, 40; *Chem. Abs.*, 1933, 27, 4904.

$$CH_4 \xrightarrow{\text{Oxidation}} CH_3OH \longrightarrow H_2C(OH)_2 \longrightarrow HCHO + H_2O$$

For hydrocarbons containing more than one carbon atom in the molecule oxidation proceeds in similar, though somewhat more complicated, steps.

This theory has been criticized because the intermediate products between the hydrocarbon and the aldehyde, particularly the primary alcohol, are extremely difficult to isolate. Bone,[59] however, found that the alcohol was more easily oxidized than the corresponding hydrocarbon under similar conditions, hence attached no significance to its absence. Nevertheless, in a few instances, the primary alcohol has been detected, for example, in the oxidation of methane with the oxides of nitrogen,[60] in the oxidation of ethane with ozone,[61] and in the slow-combustion of ethane at high pressures.[61a]

Another point in Bone's theory which has been criticized is the postulation of compounds in which two hydroxyl groups are attached to one carbon atom. This grouping has been actually demonstrated in but few compounds. In addition, the work of Wieland[62] appeared to indicate, in some instances at least, that the formation of the aldehyde from the primary alcohol takes place by dehydrogenation rather than by hydroxylation.

Callendar[63] was unable to establish the presence of any hydroxyl compounds in the oxidation of aliphatic hydrocarbons and has, therefore, objected to the hydroxylation theory on the ground that the formation of such compounds could only take place after the disruption of the oxygen molecule. This rupture of the oxygen molecule would hardly take place at the low temperatures used. Furthermore, such a breaking up of the oxygen molecules would be accompanied by ionization and no evidence of this was observed. He interpreted the results in the light of the peroxide theory.

In the peroxide theory, which is held by many of the later workers, the formation of the aldehyde is preceded by the formation of an intermediate peroxide resulting from the direct addition of a molecule of oxygen to a molecule of the hydrocarbon. The oxygen thus combined in the peroxide is held to be much more active. This mechanism is analogous to the oxidation of benzaldehyde, the peroxide of which has been isolated. Bach[64] was among the first to report the formation of such peroxides during the oxidation of petroleum distillates. Grün, Ulbrich and Wirth[65] termed such a substance a moloxide, and considered it to be an unstable peroxide. The active oxygen in a partially reacted mixture of hexane and oxygen was determined by Brunner and Rideal.[66] They established the presence of peroxides (which liberated iodine from an acid solution of potassium iodide) equivalent to 3.2 per cent of the hexane. Berl, Heise and Winnacker,[67] however, suggested that dehydrogenation preceded peroxide formation. This loss of two hydrogen atoms from the molecule results in the formation of a free radical which then combines with a molecule of oxygen to form a peroxide.

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[59] See Bone and Stockings, *J.C.S.*, 1904, 85, 693.

[60] Layng and Soukup, *Ind. Eng. Chem.*, 1928, 20, 1052.

[61] Bone and Drugman, *Proc. Chem. Soc.*, 1904, 20, 127.

[61a] Newitt and Bloch, *Proc. Roy. Soc. (London)*, 1933, **A140**, 426; *Brit. Chem. Abs.* **A**, 1933, 678; previously mentioned in footnote 4.

[62] *Ber.*, 1912, 45, 493. See also Bermejo, *Anal. Fis. Quim.*, 1929, 27, 695; *Brit. Chem. Abs.* **A**, 1930, 57.

[63] *Engineering*, 1927, 123, 147; *Brit. Chem. Abs.* **B**, 1927, 272.

[64] *Compt. rend.*, 1897, 124, 951; *Chem. Soc. Abs.*, 1897, 72 (2), 401.

[65] *Ber.*, 1920, 53, 987.

According to Mardles,[68] methane is exceptionally resistant to oxidation in air. Its temperature coefficient is low. He concluded that the oxidation of methane proceeds according to the peroxide theory, methyl hydrogen peroxide being the initial substance formed. This undergoes decomposition to methyl alcohol, formaldehyde and other products.

Further evidence for the peroxide theory was indicated by the oxidation of white oil at 120° C. for various periods of time.[69] On analysis, it was found that the peroxide value passed through a maximum and then decreased before the acetyl value (apparently signifying the formation of alcohols) reached a maximum. The saponification value also increased as the oxidation proceeded. These results were explained on the basis that peroxides are first formed, which then decompose to give alcohols and acids.

Lewis,[70] on the other hand, has criticized the peroxide theory because of the lack of conclusive proof of the formation of peroxides from saturated compounds. As an alternative, he suggested that the hydrocarbon reacts directly with oxygen to form an unsaturated compound and water. This unsaturated compound then later reacts with oxygen to yield aldehydes or peroxides.

It has been pointed out that although the peroxides of the saturated hydrocarbons have not been isolated, their formation has often been indicated.[71] Peroxide formation from unsaturated hydrocarbons, on the other hand, has been well established, and the isolation of some of these peroxides has been accomplished.[72]

From his study of the oxidation of alkylbenzenes referred to previously, Stephens [73] concluded that the formation of alcohol was not an intermediate step. He suggested that the oxidation of paraffin hydrocarbons takes place in the same way as the oxidation of the aliphatic side-chains of aromatic hydrocarbons. He therefore proposed an oxidation mechanism which involves the union of the hydrocarbon molecule with an oxygen molecule to form a complex. This complex then decomposes to yield water and an unsaturated oxygenated residue which rearranges to form an aldehyde or a ketone.

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[66] *J.C.S.*, 1928, **130**, 1162, 2824; see also, *Helv. Chim. Acta*, 1930, **13**, 197; *Brit. Chem. Abs.* **A**, 1930, 549.

[67] *Z. phys. Chem.*, 1928, **139A**, 453; *Chem. Abs.*, 1929, **23**, 965.

[68] *Trans. Faraday Soc.*, 1931, **27**, 681; *Chem. Abs.*, 1932, **26**, 1748.

[69] Yamada, *J.S.C.I.*, *Japan*, 1933, **36**, 277B; *Chem. Abs.*, 1933, **27**, 4063.

[70] *J.C.S.*, 1927, **129**, 1555.

[71] The relative merits of the peroxide and hydroxylation theories of oxidation are discussed by Bone (*Nature*, 1931, **128**, 188; *Chem. Abs.*, 1932, **26**, 1752; *Proc. Roy. Soc.* (*London*), 1932, **A137**, 243; *Chem. Abs.*, 1932, **26**, 6140; *J. Roy. Soc. Arts*, 1933, **81**, 550; *Chem. Abs.*, 1933, **27**, 3060; *J.S.C.I.*, 1933, **52**, 202T; *J.C.S.*, 1933, 1599) and by Mardles (*Nature*, 1931, **128**, 304; *Chem. Abs.*, 1932, **26**, 1752; *Trans. Faraday Soc.*, 1931, **27** (2), 681; *Chem. Abs.*, 1932, **26**, 1748; *Trans. Faraday Soc.*, 1932, **28**, 69; *Brit. Chem. Abs.* **A**, 1932, 344).

[72] Stephens, *J.A.C.S.*, 1928, **50**, 2523.

[73] This question of peroxide formation from unsaturated hydrocarbons is discussed more fully in Chapter 40.

Chapter 38

Formaldehyde and Other Aldehydes

Formaldehyde was discovered by Hofmann[1] in 1867 as one of the oxidation products of methyl alcohol. Since its industrial production from the same raw material, which started somewhat later,[2] this substance has assumed a position of increasing importance.[3] The industrial applications which have been made of it are manifold, in keeping with its enormous reactivity.

The antiseptic properties of formaldehyde are well known. This characteristic serves to explain its wide use in sterilization, disinfection, embalming, and as a preservative for tissue. Some applications have also been made of the therapeutic properties of its compound with ammonia (hexamethylenetetramine, which is also known as urotropin, hexa, formin, cystamin), or with other substances in preparations such as tannoform and "Formamint". By far the most important use of hexamethylenetetramine, however, is in the manufacture of plastics.[4] Formaldehyde has also found applications in the tanning of leather, for the hardening of gelatin and other nitrogenous material such as casein (for example, in the manufacture of the plastic called "Galalith"), in the paper and textile industries and for fixing glues and sizes. Because of its reducing action it has been employed in the recovery of silver and gold and in the silvering of mirrors. Diphenylmethane dyes of the auramine and acridine types are made by condensation of formaldehyde with aromatic amines.[5] Condensation of formaldehyde with phenol, urea, or thiourea in the presence of acids or bases yields resinous products such as "Bakelite" or "Unyte" with a wide variety of applications.[6]

Commercial formalin, a 40 per cent (by volume, 37 per cent by weight) aqueous solution of formaldehyde, is generally made by the oxidation of methyl alcohol. Methyl alcohol vapors and air, in carefully regulated quantities, are led over a contact catalyst, generally copper, and the products are then condensed. It is necessary to heat the copper at the beginning, but after the reaction is once started the heat of reaction is sufficient to keep the catalyst at an appropriate temperature (dull red heat). The condensate must be subsequently freed from excess methyl alcohol by distillation.

One of the largest sources of supply for methyl alcohol has been the wood distilleries. With the decrease in demand for wood charcoal, together with the synthetic production of methyl alcohol, particularly in Germany, this source has been curtailed. However, the greatly increased production of gaseous hydrocarbons such as coal gas, natural gas, and cracking gas has led to investigation of their suitability as raw materials for the production of formaldehyde[7] by partial oxidation. In this chapter only the partial oxidation of the gases of the saturated aliphatic series, such as methane and ethane, will be discussed, leaving the oxidation of unsaturated hydrocarbon gases for the next chapter(39).

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[1] *Ann.*, 1868, **145**, 357; *Ber.*, 1869, **2**, 152.

[2] See, for example, Trillat, French Patent 199,919, 1899; German Patent 55,176, 1889; *Chem. Zentr.*, 1891, **1**, 688. *Monit. Scient.*, 1892, 490; *J.S.C.I.*, 1892, **11**, 1025.

[3] See Orlow-Kietabl, "Formaldehyd," J. A. Barth, Leipzig, 1909.

[4] Some later applications of hexamethylenetetramine which have been proposed were in the preparation of a solid fuel (Wygodsky, U. S. Patents 1,895,955 and 1,895,956, Jan. 31, 1933; *Chem. Abs.*, 1933, **27**, 2559) and of a combustible composition ignitable by friction repeatedly after being blown out (Ringer, U. S. Patent 1,903,838, Apr. 18, 1933; *Chem. Abs.*, 1933, **27**, 3320).

[5] See, e.g., Morgan, *J.S.C.I.*, 1930, **49**, 245T.

[6] Further detailed descriptions of these resinous materials and their uses can be found in Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York.

Formaldehyde is a gas which can be condensed to a liquid boiling at —21° C. It is very soluble in water.[8] The liquid aldehyde slowly polymerizes at its boiling point.[9] The evaporation of a solution of formaldehyde yields the solid polymer known as paraformaldehyde, which melts at 150° to 160° C. Reaction of the aldehyde with ammonia to form hexamethylenetetramine, $(CH_2)_6N_4$, is characteristic. From this compound the aldehyde can be regenerated by warming with acid. With sodium bisulphite and sulphurous acid it forms addition compounds.[10] With oxidizing reagents in acid solution, it is converted to formic acid, carbon dioxide and water, but in alkaline solution formates are the principal products.

NON-CATALYTIC OXIDATION OF METHANE

Although the oxidation of methane to formaldehyde, particularly in the presence of catalysts, has been the subject of many investigations, the available information on the slow or partial oxidation of methane, on the other hand, is somewhat limited. Bone and Wheeler[11] showed that oxygen and methane in contact with a refractory surface reacted between 400° to 500° C. to give formaldehyde (yields sometimes as high as 22 per cent of the methane burned), as well as carbon monoxide and carbon dioxide. In some of their experiments they were also able to detect small quantities of formic acid. Methyl alcohol was not detected by them among the products of the slow-oxidation of methane.

Subsequent to Bone and Wheeler's studies, Blair and Wheeler[12] carried out an investigation of the slow-oxidation of methane and from their work the following conclusions were reached:

(1) The rate of thermal decomposition of methane is much slower than its rate of oxidation. Below 850° C. no complications from this source were encountered during heating periods of about 1 second.

(2) The rate of oxidation of methane is much slower than that of ethylene, so that methane requires a temperature of at least 600° C. to react at all during a short period of heating.

(3) The explosive limits of methane and oxygen are between 57 and 60 per cent of methane and the ignition temperature of methane is between 550° and 700° C.

(4) To obtain formaldehyde the heating period must be very short, decomposition beginning at 310° C.

Below 700° C. the reaction is very slow. Increasing the temperature increases the rate of reaction. For the production of formaldehyde a temperature of 720° C. appeared to be the optimum. The presence of steam increased the yield of formaldehyde. The presence of ammonia gas seemed to stabilize the formic acid, but had no great effect upon the formaldehyde. Ledbury and Blair[13] also discussed the production of formaldehyde by the controlled oxidation of methane and ethylene, arriving at similar conclusions.

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[7] Formaldehyde has also been produced by the reduction of carbon monoxide or dioxide with hydrogen; see Brodie, *Proc. Roy. Soc.*, 1872, **21**, 245; Thénard, *Compt. rend.*, 1873, **76**, 1508; Losanitch and Jovitchitsch, *Ber.*, 1897, **30**, 135; Collie, *J.C.S.*, 1901, **79**, 1063 (used $C_2H_4 + CO$); Heptinere, *Bull. acad. roy. Belg.*, 1897, **34**, 269; also Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930, 707, 675, 677.

[8] Vapor pressures of formaldehyde solutions have been determined by Blair and Ledbury, *J.C.S.*, 1925, **127**, 26.

[9] See Walker, *Ind. Eng. Chem.*, 1931, **23**, 1220.

[10] Determination and properties of these addition compounds are described by Ledbury and Taylor, *J.S.C.I.*, 1926, **45**, 85T.

[11] *J.C.S.*, 1902, **81**, 535; 1903, **83**, 1074; *cf.* Armstrong, *J.C.S.*, 1903, **83**, 1088.

[12] *J.S.C.I.*, 1923, **42**, 81T, 87T; *Chem. Abs.*, 1923, **17**, 1950.

[13] *Dept. Sci. Ind. Research* (*Brit.*) *Report* 1, 1927; *Chem. Abs.*, 1928, **22**, 574.

In their work on the slow oxidation of methane, Tropsch and Roelen[14] passed mixtures of methane and air through heated quartz tubes which contained no catalyst. The gas rate was such that the mixture was in the heated zone for a period of about 0.001 second. By varying the experimental conditions it was found that the optimum concentration of methane in the mixture was 16 per cent, and the yield of formaldehyde at 1000° C. was equivalent to 5.96 per cent of the methane used. At 700° C., however, 70 per cent of the methane actually reacting with the oxygen was converted to formaldehyde. This latter result apparently indicates that formaldehyde is the principal product of the reaction of methane and oxygen under these conditions.

The action of ozone on methane to produce formaldehyde has been studied by Wheeler and Blair.[15] Mixtures containing 97 per cent oxygen and 3 per cent methane were first passed through an ozonizer (giving approximately 4 per cent ozone) and then through a heated hard glass tube. The heating temperature varied from 15° to 400° C. and the time of contact of the gases in the hot tube was about 2½ minutes. The optimum temperature was found to be 300° C., and at this temperature 20 per cent of the methane was converted to formaldehyde. When oxygen alone was passed through the ozonizer and then mixed with methane, similar results were obtained. With a mixture of ozone, methane and ammonia, it was again found that the ammonia stabilized the formic acid that was formed, but had no effect on the formaldehyde.[16] No methyl alcohol was found in any of the experiments.

The oxidation of methane by ozone was investigated also by Wartenburg, Muchlinski and Riedler.[17] Their yields of formaldehyde, even under the most varied conditions, were small. Elworthy,[18] on the other hand, considered this type of oxidation commercially promising.

Catalytic Oxidation of Methane

One of the first processes for producing formaldehyde, together with methyl alcohol, from methane, was that of Glock.[19] In this process methane and oxygen are passed over a heated mixture of metallic copper and pumice or asbestos, and the products condensed. A mixture of coke-oven or illuminating gas and air could likewise be used.

Blackmore[20] suggested the preparation of methyl alcohol or formaldehyde by the oxidation of methane with ferro-ferric oxide (Fe_3O_4). The substance obtained depends principally upon the temperature at which the oxidation takes place. At 125° C. (260° F.) the main product of the reaction is methyl alcohol, but at 330° C. (625° F.) formaldehyde is obtained in large quantities.

A number of metals have been mentioned as catalysts.[21] In one process[22] a mixture of methane and air or oxygen (3 volumes of methane and 100 volumes of moist air) is passed over copper or silver[23] at 150° to 200° C. A portion of the methane is converted to formaldehyde, which is removed by treating the gaseous mixture with water. The residual gas is mixed with a further quantity of air, or oxygen, and again passed over the heated metal.

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[14] *Brennstoff-Chem.*, 1924, 5, 37; *Chem. Abs.*, 1924, 18, 2494.

[15] *J.S.C.I.*, 1922, 41, 331T.

[16] *Cf.* Berl and Fischer (*Z. angew. Chem.*, 1923, 36, 297; *Chem. Soc. Abs.*, 1923, 124 (1), 641), who state that stabilization of formaldehyde with ammonia indicated it to be of little value.

[17] *Z. angew. Chem.* 1924, 37, 457; *J.S.C.I.*, 1924, 43, 692B.

[18] *Can. Dept. Mines, Summary Rept.*, 1921, 586, 64; *Chem. Abs.*, 1923, 17, 2636.

[19] German Patents 109,014 and 109,015, 1898; *Chem. Zentr.*, 1900, 2, 304; see also Gruszkiewicz, Austrian Patent 7,279, 1913; *Chem. Abs.*, 1915, 9, 355. von Unruh (U. S. Patent 891,753, June 23, 1908; assigned to Sauerstoff- und Stickstoff-Industrie Hansmann and Co.) has described a "process of oxidizing methane, which consists in subjecting methane in the presence of gases containing free oxygen to the catalizing action of bark at a temperature of from 30° to 50° C."

[20] U. S. Patent 774,824, Nov. 15, 1904; *J.S.C.I.*, 1904, 23, 1237.

[21] *Cf.* Layng and Soukup, *Ind. Eng. Chem.*, 1928, 20, 1052.

[22] Verein für Chemische Industrie in Mainz, German Patent 286,731, 1913; *J.S.C.I.*, 1916, 35, 73.

A larger yield of formaldehyde may be obtained if oxidation is carried out in the presence of ammonia.[24] For example, when 6 volumes of methane, 12 volumes of oxygen (or the corresponding quantity of air) and 4 volumes of ammonia are passed through a reaction tube provided with a heated constriction the product consists principally of hexamethylenetetramine, in about 70 per cent yield. The temperature at the constriction in the tube is kept at 300° to 500° C., or at 700° C. if the reaction is conducted under reduced pressure. The tube itself or a steel tube packed at the constriction with thin silver, or nickel, or copper wire may serve as the catalyst. Formaldehyde can be easily regenerated from the hexamethylenetetramine obtained. The use of ammonia to effect the formation of hexamethylenetetramine was also described by Plauson.[25]

Carbon dioxide has also been suggested as the oxidizing agent. For example, when methane and carbon dioxide are passed through a constricted tube heated to 500° to 700° C., a 56 per cent yield of formaldehyde is procured.[26] The tube can be made of copper, silver, nickel, or alloys of these metals with one another or with tin, zinc, or aluminum. The reactions appear to be:

$$2CO_2 \longrightarrow 2CO + O_2$$

$$O_2 + CH_4 \longrightarrow HCHO + H_2O$$

Another method of oxidizing methane to formaldehyde, in which a mixture of methane and air or oxygen is passed through molten lead at 327° C., was described by Morgan.[27]

In a study of the effect of different catalysts on the oxidation of methane to formaldehyde, Schönfelder[28] observed that if methane is conducted with steam and air over copper or silver heated to 500° C., about 55 to 58 per cent is oxidized to formaldehyde, 25 to 40 per cent remains unattacked, and 10 to 20 per cent burns to carbon monoxide, carbon dioxide and water.

Medvedev[29] used gold, platinum, manganous oxide, nickelous oxide, aluminum oxide, cupric oxide, silver oxide, lead oxide (PbO) and ceric oxide catalysts dispersed on an asbestos base. At low gas-flow rates and low temperatures (250° to 350° C.) only carbon dioxide formed. By working at temperatures above 500° C. with a copper catalyst and increasing the gas-flow rate twenty-fold, he was able to obtain, in addition to carbon dioxide, a small quantity of carbon monoxide and a trace only of formaldehyde. At 600° C., however, the use of glass gave a large yield of formaldehyde. This was attributed to the lesser chemical activity of the glass surface. The use of lead catalysts (borate or phosphate or their mixtures) gave high yields of formaldehyde at 500° to 700° C. when the methane carried 3 to 7 per cent hydrogen. The activity of these catalysts, however, was probably due to the presence of volatile impurities, such as lead chloride or hydrogen chloride, as other experiments showed increased yields of formaldehyde when a small quantity (0.13 per cent) of hydrogen chloride was present during oxidation. Medvedev[30] also employed tin borate and phosphate, which were heat-resistant at the reaction temperature.

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[23] Day (U. S. Patent 1,871,117, Aug. 9, 1932; *Chem. Abs.*, 1932, **26**, 5572) used a mixture of silver or copper oxide with a small portion of rare earth oxide such as that of samarium. *Cf.* I. G. Farbenindustrie A.-G.; British Patent 355,308, 1930; *Brit. Chem. Abs.* **B**, 1931, 1036.

[24] H. O. Traun's Forschungslaboratorium A.-G., British Patent 156,136, 1920; *J.S.C.I.*, 1922, **41**, 437A; *cf.* Blair and Wheeler, *J.S.C.I.*, 1923, **42**, 81T; Wheeler and Blair, *J.S.C.I.*, 1922, **41**, 331T; *Chem. Abs.*, 1923, **17**, 58.

[25] Canadian Patent 227,884, 1923; *Chem. Abs.*, 1923, **17**, 1241.

[26] H. O. Traun's Forschungslaboratorium G.m.b.H., British Patent 156,148, 1922; *J.S.C.I.*, 1922, **41**, 438A.

[27] British Patent 176,438, 1920; assigned to Thermal Industrial and Chemical Research Co., Ltd.; *J.S.C.I.*, 1922, **41**, 315A.

[28] *Ber. Ges. Kohlentechnik*, 1923. (IV) 247; *Chem. Abs.*, 1924, **18**, 1271.

[29] *Trans. Karpov. Inst. Chem.*, 1924, **3**, 54; *Chem. Abs.*, 1927, **21**, 2457.

A stripped natural gas (containing 1 to 5 per cent air, 0,1 per cent carbon dioxide, 52 to 56 per cent methane, 10 to 12 per cent ethane, 17 to 20 per cent propane and 10 to 12 per cent higher hydrocarbons) was oxidized by air in the presence of various catalysts by Korovatzki.[31] Nitrogen dioxide had scarcely any catalytic activity and copper caused considerable decomposition. Up to 32 per cent of liquid oxidation products, consisting of alcohols, aldehydes, and acids, were formed by oxidation with oxygen, the yield depending upon the concentration of the latter and the rate of flow. The formaldehyde in the condensate corresponded to 10 per cent of the total or 2 to 3 per cent of the charge. Temperatures of 600° to 700° C. caused oxidation to water, carbon dioxide and unsaturated compounds.

The oxides of molybdenum, vanadium, manganese, tungsten, uranium, chromium, titanium and zirconium, or mixtures of these oxides with silver oxide, have been used as catalysts by James.[32] Methane with 1 to 3.5 volumes of air is passed over such catalysts at 550° C., the period of contact being about 1 second. Both formaldehyde and formic acid are produced, the yield of the former being about 6.75 per cent based on the methane used. It is advantageous to use several reaction chambers in series, and to remove the reaction products between successive chambers. This process is applicable not only to methane, but also to coal gas and to petroleum still gases. The products from the latter, however, consist of a mixture of aldehydes and acids. It is also possible to substitute ozonized air in place of air.

For the oxidation of natural gas, or other gases, containing a high percentage of methane, Boomer[33] proposed mixtures of zinc and lead chromates. A mixture of natural gas and oxygen, under pressures of 60 to 300 atmospheres, is passed over these catalysts at 250° to 500° C.

In the United States the production of formaldehyde and other aldehydes as well as alcohol was undertaken for a considerable period by the Empire Gas and Fuel Company. Natural gas, or gases from the distillation of coal, petroleum or shale, were mixed with air, oxygen or carbon dioxide and allowed to react in the presence of a catalyst at 425° to 485° C. (800° to 900° F.). Aldehydes and alcohols were obtained together with a gas of more uniform calorific power.[34] Platinum, palladium, gold, silver, copper, chromium, manganese, iron or nickel or their oxides could be used as catalysts. The reacting substances were maintained under a pressure of 100 to 300 pounds. By varying the conditions and catalysts it was possible to carry out the oxidation in stages. For example, methane in one stage could be oxidized to methanol, and in another to formaldehyde; or ethane could be oxidized in one stage, and methane in another.

OXIDATION OF METHANE WITH GASEOUS CATALYSTS

The oxidation of methane in the presence of gaseous catalysts in place of metallic or metallic oxide catalysts has also received some attention. The most important of these gaseous catalysts are the oxides of nitrogen, particularly nitrogen dioxide, though chlorine, sulphur dioxide, sulphur trioxide, and hydrogen chloride have been used also.

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[30] Russian Patent 3,605, 1927; *Chem. Abs.*, 1928, **22**, 4740.

[31] *Neft. Khoz.*, 1931, **20**, 483; *Chem. Abs.*, 1932, **26**, 4029.

[32] U. S. Patent 1,588,836, June 15, 1926; *Chem. Abs.*, 1926, **20**, 2582; U. S. Patent 1,675,029, Jan. 26, 1928; *Brit. Chem. Abs.* B, 1928, 633.

[33] U. S. Patent 1,776,771, Sept. 30, 1930; Canadian Patent 291,411, 1929; *Chem. Abs.*, 1929, **23**, 5308; both patents assigned to the Governors of the University of Alberta.

[34] Walker, British Patent 290,613, 1927; *Chem. Abs.*, 1929, **23**, 846; British Patent 295,356, 1927; *Chem. Abs.*, 1929, **23**, 2186; Canadian Patent 300,567, 1930; *Chem. Abs.*, 1930, **24**, 3516; all assigned to Empire Gas and Fuel Co.

One of the first methods in which nitrogen dioxide was used was described by Bailey.[35] In this process one volume of methane, or its equivalent in the form of natural gas, or any other gas having a high methane content, is mixed with two volumes of nitric oxide and sufficient oxygen, or air, to convert the nitric oxide to nitrogen dioxide. The mixture of gases is then passed through a tube heated to 450° C. The tube may be made of porcelain or any other material which is not affected by the gases. The reaction products are quickly brought into contact with an aqueous sludge of calcium carbonate which unites with the oxides of nitrogen, except nitric oxide, and thus prevents the further oxidation of formaldehyde to carbon dioxide and water. The solid portions of the sludge are removed by filtration and the formaldehyde in solution is recovered by distillation.

In the process developed by Bibb[36] the quantity of nitric oxide used is much smaller (1 to 2 per cent), and it acts more as a carrier or a catalyst. The mixture of methane or natural gas and oxygen is further mixed with air which has been passed through nitric acid and which, therefore, contains some of the oxides of nitrogen. This mixture of methane, air, and nitrogen oxides is preheated to 200° C., passed through a reaction chamber kept at a temperature of 250° to 560° C., and then through a scrubber. The aldehyde is recovered in the usual manner and the residual gases are used again. The presence of only small proportions of nitric oxide is an aid in controlling the extent of oxidation.

Somewhat later, Bibb and Lucas[37] modified the operation by first passing the methane through concentrated nitric acid after which it was mixed with 3.5 to 7 volumes of air. The resulting mixture was heated at 700° to 750° C. It was observed that the highest concentration of formaldehyde in the condensate was obtained with a furnace temperature of 750° C., a time of contact of 0.13 second, and a low air-hydrocarbon ratio. In a later investigation, Bibb[38] obtained yields as high as 7.42 pounds of 40 per cent formaldehyde solution from 1 pound of nitrogen dioxide and about 390 cubic feet of natural gas.

Both gaseous and solid catalysts have been used simultaneously. Harter[39] made oxides of nitrogen by passing a mixture of nitrogen and oxygen into a quartz tube through which a high tension arc is conducted. Hydrocarbon gases, particularly methane, are then added to the mixture of oxygen and nitrogen oxides and the resulting gas is passed through a heated reaction chamber which contains catalysts of copper, silver, cobalt or manganese dispersed on silica gel. Activated carbon can also be used. The reaction products are quickly cooled and recovered.

From a study of the oxidation of methane with nitrogen dioxide Frolich, Harrington and Waitt[40] found that the minimum temperature for reaction in an open pyrex tube is about 430° C. The yield of formaldehyde was less than 25 per cent of the methane reacting and methyl alcohol could not be detected. The conditions which favor formaldehyde production are: low concentration of nitrogen dioxide, slow rate of flow of the reactants, and the absence of reacting surfaces. Attention was also called to the possible formation of acetic acid by the reaction of liquid nitrogen dioxide with higher hydrocarbons of the methane series. Smith and Milner[41] concluded, from their work on the oxidation of methane with nitrogen dioxide in quartz tubes at 500° to 700° C., that the production of formaldehyde under such conditions was too small to be commercially feasible.[42]

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[35] U. S. Patent 1,319,748, Oct. 28, 1919; *Chem. Abs.*, 1920, **14**, 71.

[36] U. S. Patent 1,392,886, Oct. 4, 1921; *Chem. Abs.*, 1922, **16**, 424; Re-issue 15,789, Mar. 11, 1924. Canadian Patent 302,672, 1930; *Chem. Abs.*, 1930, **24**, 4519. See also Layng and Soukup, *Ind. Eng. Chem.*, 1928, **20**, 1052.

[37] *Ind. Eng. Chem.*, 1929, **21**, 633.

[38] *Ind. Eng. Chem.*, 1932, **24**, 10.

[39] Harter, British Patent 337,407, 1929; *Brit. Chem. Abs.* **B**, 1931, 54. Gutehoffnungshütte Oberhausen A.-G., British Patent 375,314, 1932; *Chem. Abs.*, 1933, **27**, 3951; French Patent 709,823, 1931; *Chem. Abs.*, 1932, **26**, 1302.

[40] *J.A.C.S.*, 1928, **50**, 3216; *Brit. Chem. Abs.* **A**, 1929, 289.

Carman[43] proposed the addition of chlorine to the gaseous mixture of methane and oxygen, and also the use of such catalysts as barium, calcium, or strontium chloride at temperatures of 400° to 500° C. A large yield of formaldehyde was obtained, probably because the chlorinated products, which are first formed, are more easily oxidized than methane itself. The reactions which appear to take place have been represented as follows:

$$2CH_4 + 2Cl_2 \longrightarrow 2CH_3Cl + 2HCl$$
$$2CH_3Cl + O_2 \longrightarrow 2CH_2O + 2HCl$$
$$4HCl + O_2 \longrightarrow 2H_2O + 2Cl_2$$

The hydrogen chloride and formaldehyde are absorbed in water, from which the formaldehyde may be obtained as its solid polymer by cooling to a point where polymerization and precipitation is rapid.

The possibility of partially oxidizing methane with sulphur dioxide or sulphur trioxide in the presence of silica as a catalyst and at temperatures of 250° to 800° C. was investigated by Berl and Fischer.[44] No formaldehyde was obtained with sulphur dioxide, most of the methane being oxidized to carbon dioxide. With sulphur trioxide and a large excess of methane, about 0.5 per cent of the methane was converted to formaldehyde, no other oxidation products being observed. When using air alone it was reported that 1.8 per cent of the methane was converted to formaldehyde, 32.4 per cent to carbon monoxide, 3.45 per cent to carbon dioxide, and 63.35 per cent remained unchanged.

CATALYTIC OXIDATION OF METHANE BY SILENT ELECTRIC DISCHARGE

An investigation of the catalytic oxidation of methane with a silent electric discharge employing a number of metallic oxide catalysts was made by Elworthy.[45] Oxidation of mixtures of methane and oxygen by this means yielded a viscous liquid which contained polymerized aldehydes, resins, methyl alcohol, formaldehyde, and formic acid. This process was considered to possess possible commercial interest.

Kloppenburg[46] proposed to make methyl alcohol and formaldehyde by treating a mixture of methane and oxygen in the presence of activated coconut carbon with the dark electric discharge. During the operation of this process the apparatus is cooled to keep the temperature below 35° C.

Formaldehyde has been prepared by passing a mixture of air or oxygen and methane through the field of a high frequency and high voltage current.[47] Catalysts such as copper or silver may be used.[48] The gases issuing from the apparatus are washed to remove the formaldehyde. Yields of from 350 to 480 grams of formaldehyde are realized from 1 cubic meter of methane. Other catalysts such as calcium or magnesium carbonates,[49] quartz,[50] metals or their oxides and nitrogen oxides[51] can also be employed. The methane may be mixed with steam. Hexamethylenetetramine is formed due to the action of the nitrogen of the air and can be removed by washing.

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[41] *Ind. Eng. Chem.*, 1931, **23**, 357.

[42] *Cf.* Korovatzki, *loc. cit.*

[43] U. S. Patent 1,697,105, Jan. 1, 1929; *Chem. Abs.*, 1929, **23**, 1142. Also Carman and Chilton, U. S. Patent 1,697,106, Jan. 1, 1929; *Chem. Abs.*, 1929, **23**, 1142.

[44] *Z. angew. Chem.*, 1923, **36**, 297; *Chem. Abs.*, 1924, **18**, 968.

[45] *Trans. Roy. Soc. Canada*, 1922, **16** (3), 93; *Chem. Abs.*, 1923, **17**, 2042. See also Chance, U. S. Patent 1,298,889, Apr. 1, 1919.

[46] U. S. Patent 1,500,080, July 1, 1924; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1925, **19**, 78.

[47] Nashan, U. S. Patent 1,909,215, May 16, 1933; assigned to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1933, **27**, 3675.

When carbon dioxide and methane are treated with high frequency currents both formaldehyde and acetaldehyde result.[52] The same catalysts which can be used in the oxidation of methane likewise promote this reaction, i.e., calcium or magnesium carbonate, or quartz glass.

OXIDATION OF HIGHER HYDROCARBONS TO ALDEHYDES

Bone and Stockings[53] observed that during slow-combustion, ethane was oxidized much more rapidly than methane. Mixtures of ethane and oxygen in borosilicate glass tubes were heated to 250° to 400° C. under pressures of 1.75 to 2.33 atmospheres, or to 400° to 500° C. under reduced pressures in a "circulation apparatus." The products were carbon monoxide and dioxide, water, traces of formic acid and acetaldehyde, and a relatively large quantity of formaldehyde. The absence of ethyl alcohol and any large quantity of acetaldehyde is explained by the hydroxylation theory.[54]

In the partial oxidation of ethane and propane, formaldehyde is the oxygenated product obtained in the greatest quantity. Curme[55] carried out the oxidation at temperatures above 600° C. (generally 700° to 710° C.), using a silica heating surface as the catalyst. The gases leaving the reaction chamber are scrubbed with cold water to remove the formaldehyde, and the residual gases are recirculated. In addition to formaldehyde, higher aldehydes are obtained in small amounts. Thus, with ethane, some acetaldehyde is also produced. Another procedure consists in heating the hydrocarbons (ethane and propane) to 700° C. in the absence of air (which is termed the "degradation" treatment) and then introducing air.[56] The yield of formaldehyde is about 85 per cent.

Working with the liquid hydrocarbons, Stepski[57] passed a stream of air, saturated with the vapors of the hydrocarbon, over glowing platinum. The products were then cooled to -15° C., and the uncondensed gases led into bromine. His qualitative results showed that isopentane yields formaldehyde and ethylene in large quantities, together with propylene, the three isomeric butylenes, two isoamylenes, carbon dioxide, and water, whereas n-hexane gives formaldehyde and ethylene, together with propylene, 1- and 2-butene, two amylenes, three hexylenes, carbon dioxide, and water.

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[48] Gutehoffnungshütte Oberhausen A.-G., British Patent 343,461, 1928; *Brit. Chem. Abs.* **B**, 1931, 621; French Patent 687,735, 1930; *Chem. Abs.*, 1931, **25**, 715; British Patent 352,978, 1930; *Brit. Chem. Abs.* **B**, 1931, 1086.

[49] Gutehoffnungshütte Oberhausen A.-G., British Patent 353,076, 1929; *Chem. Abs.*, 1932, **26**, 3446; French Patent 694,382, 1930; *Chem. Abs.*, 1931, **25**, 1844; French Patent 694,330, 1930; *Chem. Abs.*, 1931, **25**, 1744.

[50] Gutehoffnungshütte Oberhausen A.-G., British Patent 353,455, 1929; *Chem. Abs.*, 1932, **26**, 3446.

[51] Gutehoffnungshütte Oberhausen A.-G., British Patent 375,314, 1931; *Brit. Chem. Abs.* **B**, 1932, 972.

[52] Gutehoffnungshütte Oberhausen A.-G., British Patents 353,076 and 353,455, 1930; *Chem. Abs.*, 1932, **26**, 3446. Finlayson and Plant, British Patent 364,023, 1930; assigned to British Celanese, Ltd.; *Chem. Abs.*, 1933, **27**, 1580; Dreyfus, French Patent 715,031, 1931; *Chem. Abs.*, 1932, **26**, 1525.

[53] *J.C.S.*, 1904. **85**, 710.

[54] See Chapter 37.

[55] U. S. Patent 1,729,711, Oct. 1, 1929; assigned to Carbide and Carbon Chemicals Corp.; also British Patent 238.938, 1924; *Chem. Abs.*, 1926, **20**, 2066.

[56] Carbide and Carbon Chemicals Corp., German Patent 563,874, 1924; *Chem. Abs.*, 1933, **27**, 1012.

[57] *Monatsh.*, 1902, **23**, 773; *Chem. Soc. Abs.*, 1903, **84** (1), 61.

Wheeler and Blair[58] carried out the slow-oxidation of hexane vapors at 480° to 590° C. in glass tubes in the absence of catalysts. The products which were isolated included higher aldehydes, formaldehyde, unsaturated hydrocarbons, acids (in small quantities), carbon monoxide and dioxide, water, and hydrogen (at the higher temperatures). Excess oxygen was found to increase the proportion of higher aldehydes as well as of carbon dioxide. Increase in temperature decreased the percentage of higher aldehydes formed, but increased the proportion of formaldehyde and unsaturated hydrocarbons, ethylene forming a large proportion of the latter. The quantities of carbon monoxide and dioxide also increased with increasing temperatures. No saturated hydrocarbons, it was stated, are formed, which indicates that no thermal decomposition of hexane (which would give considerable methane) takes place throughout the temperature range of these experiments.

In oxidizing boiling hexane with ozone, Blair, Wheeler and Ledbury[59] reported that formaldehyde and acetaldehyde were produced in relatively large proportions, together with much smaller proportions of higher aldehydes; some acids, principally hexanoic; traces of water and carbon monoxide and dioxide. Some esters were also present, probably mostly hexyl hexanoate. The higher aldehydes were not found in quantity due, no doubt, to the ease with which oxidation to acetaldehyde takes place.

Higher aldehydes are also made by oxidizing petroleum oils. Oxidation processes of this kind, however, result in the formation of a mixture of different aldehydes, alcohols, and acids, which are discussed more fully in succeeding chapters. As an example, the work of Schulz[60] is of interest. By passing a rapid stream of air through Boryslaw oils heated to 300° C. in a retort which was connected to a series of wash bottles, formaldehyde, acrolein, and other aldehydes, together with other products were obtained.

CATALYTIC OXIDATION OF ALCOHOLS

As previously mentioned, the first methods for the production of formaldehyde were dependent upon the oxidation of methyl alcohol.[61] Blackmore[62] led the vapors of methyl alcohol and air through a series of electrically heated copper screens. Other alcohols than methyl could be used. Fokin[63] obtained better yields of formaldehyde by placing silver in front of the copper catalyst and using a volume of air which contained the stoichiometrical quantity of oxygen. Jaeger[64] employed a metal oxide which is not easily reduced by hydrogen, such as the oxides of the alkalies or alkaline earths, together with compounds of molybdenum or vanadium. A combustion retarder, such as potassium oxide and manganese oxide, has been added to the vanadium oxide catalyst by Craver.[65]

Kuss[66] conducted a mixture of air and the vapors of anhydrous methyl alcohol over a silver catalyst at 500° C. The quantity of air used contains the theoretical quantity of oxygen required for oxidation. A 60 per cent solution of formaldehyde is thus obtained. In solutions of such concentrations the formaldehyde slowly polymerizes to the solid, paraformaldehyde. This polymerization can be hastened by slightly warming the solution. By evaporating under reduced pressure, paraformaldehyde can be separated. The hot gases from the reaction can be used for this evaporation.

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[58] *J.S.C.I.*, 1923, **42**, 491T.

[59] *J.S.C.I.*, 1924, **43**, 287T; *Chem. Abs.*, 1925, **19**, 36.

[60] *Eighth Int. Cong. of Appl. Chem.*, 1912, **10**, 273; *Chem. Abs.*, 1912, **6**, 3177.

[61] A review of these early methods is given in Thorpe, "Dictionary of Applied Chemistry," Longmans, Green and Co., New York, 1912, **2**, 592; Orlow-Kietabl, *op. cit.*

[62] U. S. Patent 868,320, Oct. 15, 1907; *J.S.C.I.*, 1907, **26**, 1215.

[63] *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 286; *Chem. Abs.*, 1913, **7**, 2227.

[64] U. S. Patent 1,709,853, Apr. 23, 1929; *Chem. Abs.*, 1929, **23**, 2721; U. S. Patent 1,735,763, Nov. 12, 1929; *Chem. Abs.*, 1930, **24**, 625; both patents assigned to Selden Co.; Meharg and Adkins, German Patent 575,767, 1933, and German Patent 575,596, 1933; *Chem. Abs.*, 1933, **27**, 4819; U. S. Patents 1,913,404 and 1,913,405, June 13, 1933; *Chem. Abs.*, 1933, **27**, 4252; all patents assigned to Bakelite Corporation.

[65] U. S. Patent 1,851,754, Mar. 29, 1932; assigned to Weiss and Downs, Inc.; *Chem. Abs.*, 1932, **26**, 2990.

[66] U. S. Patent 1,666,708, Apr. 17, 1928; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1928, 362.

Acetaldehyde was made in much the same manner by Woolcock,[67] from ethyl alcohol and air, except that some steam is mixed with the alcohol vapors and the quantity of air used contains somewhat less (about 75 per cent) oxygen than that theoretically required for the production of the aldehyde.

The activity of the copper catalyst used in the oxidation of alcohols can be increased in two ways: (1) by dispersing it on pumice, and (2) by mixing it with small quantities of rare earth oxides, such as samarium oxide.[68] The first method appears to give better yields of aldehydes from both methyl and ethyl alcohol. In the second method, however, the samarium oxide promoted the activity of the catalyst to such an extent that oxidation beyond the aldehyde stage occurred and very much lower yields of aldehydes were obtained. The second method would, as is stated, therefore be of no advantage with methyl and ethyl alcohols, but might be with substances which were somewhat more difficult to oxidize. It is believed that the presence of the rare earth oxides minimizes poisoning of the catalyst and thus greatly increases its life. The addition of silver, cobalt, zinc oxide or manganese oxide to a copper catalyst for the oxidation of ethyl alcohol to acetaldehyde has also been proposed.[69]

For the catalytic oxidation of both aromatic and aliphatic alcohols Maxted and Coke[70] found that metallic vanadates, heated to 300° C., could be used as catalysts. The best of these appeared to be tin vanadate. They are particularly applicable to the production of acetaldehyde from ethyl alcohol. Silver catalysts[71] have also been used for the oxidation of ethyl alcohol to acetaldehyde. That form of catalyst which has the greatest coefficient of heat transfer gives the highest yield of aldehyde from alcohol, according to Faith and Keyes.[72] They obtained higher yields of acetaldehyde with both copper and silver than had been reported previously.

When the vapors of butyl alcohol are passed over copper oxide heated to 260° to 320° C. there is obtained a mixture of butyl alcohol, butyl butyrate and butyraldehyde.[73] The aldehyde and ester can be separated by fractionation. The aldehyde may be further oxidized to butyric acid[74] by passing the liquid, containing about 0.5 per cent manganese butyrate, through a tower countercurrent to a stream of air.

Simington and Adkins[75] investigated the oxidation of ethyl, isopropyl and butyl alcohols by air in the presence of silver, nickel, copper, and platinum gauzes; copper wire; silver pellets; pellets of alloys of copper with zinc, nickel, bismuth, palladium, platinum, gold and manganese; mixtures of the oxides of uranium and copper, tungsten and copper, molybdenum and copper, and vanadium, iron and copper. Silver and silver-copper alloys produced yields of aldehydes and ketones in excess of 70 per cent of the theoretical. With all catalysts, butyl alcohol formed a small proportion of ester and with the mixed oxide catalysts, some formaldehyde. Ethyl alcohol gave 3 times as much carbon dioxide as butyl alcohol and twice as much as propyl alcohol.

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[67] British Patent 325,105, 1929; assigned to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1930, 409.

[68] Lowdermilk and Day, *J.A.C.S.*, 1930, **52**, 3535; *cf.* also, Day, U. S. Patent 1,871,117, Aug. 9, 1932; *Chem. Abs.*, 1932, **26**, 5572.

[69] Soc. d'études scientifiques et d'enterprises industrielles, French Patent 707,132, 1930; *Chem. Abs.*, 1932, **26**, 478.

[70] British Patent 238,033, 1924; *Chem. Abs.*, 1926, **20**, 1814.

[71] Krause, U. S. Patent 1,581,641, Apr. 20, 1926; *Chem. Abs.*, 1926, **20**, 1813.

[72] *Ind. Eng. Chem.*, 1931, **23**, 1250.

[73] Legg and Bogin, U. S. Patent 1,580,143, Apr. 13, 1926; assigned to Commercial Solvents Corporation; *Chem. Abs.*, 1926, **20**, 1813.

[74] Hancock, U. S. Patent 1,580,137, Apr. 13, 1926; assigned to Commercial Solvents Corporation; *Chem. Abs.*, 1926, **20**, 1813.

[75] *J.A.C.S.*, 1928, **50**, 1449.

OXIDATION OF ALDEHYDES

The oxidation of acetaldehyde to acetic acid has been applied industrially. At the Shawinigan Falls plant[76] of Shawinigan Chemicals, Ltd., acetylene is hydrated to acetaldehyde in the presence of mercury.[77] The acetaldehyde is then oxidized to acetic acid with air in the presence of manganese acetate at a temperature of 60° C. and a pressure of about 4.5 atmospheres.

The oxidation of acetaldehyde has been studied by Hatcher, Steacie and Howland.[78] They observed that the main reaction was of the chain type and that acetaldehyde, on coming into contact with air, forms a compound which in water behaves as an organic peroxide.[79] A number of catalysts have been proposed for the oxidation of acetaldehyde, including manganese, iron, cobalt, chromium, and copper,[80] or active carbon charged with zinc oxide and phosphoric acid.[81]

Formaldehyde may be formed by the partial oxidation of acetaldehyde.[82] The extent to which such action takes place is determined by the time of contact which, in turn, is regulated by conducting oxygen and acetaldehyde vapors through capillary tubes heated for a small portion of their length.

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[76] See Cadenhead, *Chem. Met. Eng.*, 1933, **40**, 184.

[77] These methods for the preparation of acetaldehyde are discussed in Chapter 28.

[78] *Can. J. Research*, 1931, **5**, 648; *Chem. Abs.*, 1932, **26**, 1576; *Can. J. Research*, 1932, **7**, 149; *Brit. Chem. Abs.* **A**. 1932, 1210.

[79] *Cf.* von Braun and Keller, *Ber.*, 1933, **66B**, 215.

[80] See Kagan and Morozov, *J. Applied Chem.* (*U.S.S.R.*), 1932, **5**, 400; *Chem. Abs.*, 1933, **27**, 269. Consortium für Elektrochemische Industrie G.m.b.H., French Patent 722,190, 1931; *Chem. Abs.*, 1932, **26**, 4067; British Patent 373,893, 1931; *Brit. Chem. Abs.* **B**, 1932, 832; Nippon Chissohiryo Kabushi-Kaisha, British Patent 359,878, 1930; *Chem. Abs.*, 1933, **27**, 311. Holzverkohlungs Industrie A.-G., British Patent 347,323, 1929; French Patent 687,789, 1930; *Chem. Abs.*, 1931, **25**, 714, Jochheim, German Patents 509,020, 1926, and 524,716, 1927; *Chem. Abs.*, 1931, **25**, 714, 4012; German Patent 533,466, 1927; *Chem. Abs.*, 1932, **26**, 480; U. S. Patent 1,828,372, Oct. 20, 1931; *Chem. Abs.*, 1932, **26**, 737; French Patent 36,583, 1929; *Chem. Abs.*, 1930, **24**, 5768; British Patent 321,241, 1930; *Chem. Abs.*, 1930, **24**, 2474; British Patent 329,867, 1929; *Chem. Abs.*, 1930, **24**, 5768; British Patent 364,255, 1930; all patents assigned to I. G. Farbenindustrie A.-G.

[81] Eberhardt, German Patent 554,784, 1930; German Patent 544,691, 1930; *Chem. Abs.*, 1932, **26**, 5971, 3521; both patents assigned to I. G. Farbenindustrie A.-G.

[82] Herrmann and Baum, U. S. Patent 1,864,541, June 28, 1932; assigned to Consortium für elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1932, **26**, 4343.

Chapter 39

Oxidation of Unsaturated Hydrocarbons

Olefins are generally considered to react more rapidly with oxidizing agents than do the corresponding saturated hydrocarbons.[1] This oxidation, however, need not necessarily involve a scission of the molecule as olefins yield intermediate products such as peroxides, alcohols and ozonides. The formation of gum in light petroleum distillates, made by the cracking of the heavier fractions, has been attributed to the presence of olefins which readily unite with oxygen of the air to form peroxides. These latter substances yield gum on evaporation of the gasoline. The rates of oxidation of olefins vary widely. The monolefins are less rapidly oxidized than diolefins, the latter appearing to be chiefly responsible for the gum in gasoline (see Chapter 40).

Oxidation of unsaturated hydrocarbons with dilute permanganate solution (either neutral or alkaline) often results in the addition of two hydroxyl groups at the double bond to give the corresponding glycol. Further oxidation with permanganate causes a rupture of the molecule at the double bond with the formation of acids. Identification of the acids is frequently helpful in determining the constitution of the original hydrocarbon. Occasionally, however, as in the case of some cyclic unsaturated compounds, the break in the molecule does not occur at the double bond.

Oxidation with ozone also frequently indicates the position of the double bond in the hydrocarbon molecule. Unsaturated compounds unite with ozone to form ozonides which can be hydrolyzed to give aldehydes or ketones and hydrogen peroxide, rupture of the molecule simultaneously taking place at the double bond. From the identification of the aldehydes or ketones it is possible to determine the structure of the original hydrocarbon.[2]

The largest source of unsaturated hydrocarbons is, of course, the cracking of heavy petroleum distillates. Unsaturated hydrocarbons are prepared also by the oxidation (or what probably better corresponds to dehydrogenation) of saturated or paraffin hydrocarbons. Before considering the oxidation reactions of olefins and acetylene it is of interest to discuss briefly the production of such compounds by the oxidation of petroleum hydrocarbons. Methods for preparing unsaturated hydrocarbons from paraffins by thermal decomposition or by oxidation with steam are given in Chapters 4 and 10, respectively.

Production of Unsaturated Hydrocarbons by Oxidation

This type of oxidation requires much more closely regulated conditions than the slow combustion of saturated hydrocarbons to aldehydes and acids. For example, acetylene is obtained by heating mixtures of methane and air or oxygen for very short periods of time (about 0.005 second) at 1000° to 1600° C.,[3] the short period of heating preventing action of the steam formed on the unsaturated hydrocarbon.[4] The yield of acetylene appears to depend primarily upon the temperature and the time of contact. At 1400° C. and with about 0.006 second contact, 30 per cent of the methane is converted to acetylene, and at 1600° C. and 0.001 second contact, the conversion is 50 to 60 per cent. Decreasing the pressure does not appear to increase the yield of acetylene but does favor the production of the oxides of carbon and water. Subjecting gaseous hydrocarbons to incomplete combustion at 700° to 1100° C., under pressures of 0.5 to 5 atmospheres, and in the presence of a catalyst containing free silicon also yields acetylene.[5] Or mixtures of saturated hydrocarbons and oxygen may be diluted with steam and heated to 1300° C. or higher.[6]

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[1] Estrade (*Ann. combustible liquides*, 1933, **8**, 484; *J. Inst. Pet. Tech.*, 1933, **19**, 413A) stated that, during the oxidation of saturated hydrocarbons, cyclicization does not greatly increase the resistance of the hydrocarbon to oxidation but the introduction of a double bond into the molecule does.

[2] Verley (*Bull. soc. chim.*, 1928, **43**, 854; *Chem. Abs.*, 1929, **23**, 595) pointed out that rearrangement of certain types of ozonides is possible and decomposition on hydrolysis may not therefore take place at the position originally occupied by the double bond.

In another process, methane or other gaseous hydrocarbons together with oxygen are heated to temperatures of about 1000° C., using porous or refractory ceramic materials as catalysts.[7] In some instances a gas containing 50 per cent oxygen gives better results than oxygen alone. This procedure is also applicable to tars, petroleum residues and other similar products. For instance, coal tar is heated to 250° C. and the vapors mixed with oxygen are passed through a tube containing refractory material heated to 800° C. The reaction products consist of ethylene, propylene and butylene.

The vapors of gasoline, kerosene or lubricating oils are converted to acetylene by flames of oxygen or air burning in them.[8] The yield is increased if the flame jets are of small diameter arranged in a group, rather than separate jets of a large diameter.

Ethylene is made by the careful oxidation of ethane with air or oxygen, mixed with coke-oven or water gas. This is effected by heating the gaseous mixture to temperatures of 600° to 900° C. in contact with pumice or silica.[9] Spindler[10] obtained ethylene from methane and oxygen by a process which requires two steps. The methane and oxygen is first passed over heated copper to yield formaldehyde. This substance is then made to react with more methane at 500° C. under 1000 atmospheres pressure to give water and ethylene. The catalysts employed in the second step consist of various compounds of iron, nickel, cobalt, platinum and copper. In the presence of zinc chloride, at this same temperature and pressure, ethylene undergoes polymerization and yields pentane and hexane together with unsaturated aliphatic and cyclic hydrocarbons.

Ethylene and other olefinic hydrocarbons are formed when natural gas or coal gas is mixed with air and the heated mixture passed over metallic catalysts. The catalysts can be platinum black, or the oxides of iron, copper, nickel, chromium and other metals. These unsaturated gaseous hydrocarbons may be further converted to liquid hydrocarbons by conducting the heated gases over a nickel catalyst.[11]

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[3] Fischer and Pichler, *Brennstoff-Chem.*, 1930, 11, 501; *Chem. Abs.*, 1931, **25**, 796; *Brit. Chem. Abs.* **B**, 1931, 230.

[4] Fischer and Pichler, German Patent 553,178, 1930; *Chem. Abs.*, 1932, **26**, 4611; French Patent 719,035, 1931; *Chem. Abs.*, 1932, **26**, 3261.

[5] I. G. Farbenindustrie A.-G., German Patent 536,361, 1929; *Chem. Abs.*, 1932, **26**, 999; British Patent 347,407, 1930; *Brit. Chem. Abs.* **B**, 1931, 711; British Patent 347,493, 1930; *Brit. Chem. Abs.* **B**, 1931, 662.

[6] Voituron, British Patent 349,067, 1929; *Chem. Abs.*, 1932, **26**, 5314; British Patent 352,280, 1929; *Brit. Chem. Abs.* **B**, 1931, 960; both patents assigned to Soc. d'études scientifiques et d'entreprises industrielles.

[7] I. G. Farbenindustrie A.-G., British Patent 265,234, 1926; *Chem. Abs.*, 1928, **22**, 243; British Patent 267,155, 1926; *Chem. Abs.*, 1928, **22**, 1164.

[8] Millar, U. S. Patent 1,896,552, Feb. 7, 1933; *Chem. Abs.*, 1933, **27**, 2696; Canadian Patent 309,544, 1931; British Patent 364,418, 1931; *Brit. Chem. Abs.* **B**, 1932, 248; French Patent 713,012, 1930; *Chem. Abs.*, 1932, **26**, 1624; U. S. and Canadian patents assigned to Shell Development Co.; British and French patents assigned to Bataafsche Petroleum Maatschappij.

[9] Compagnie de Bethune, British Patent 308,200, 1928; *Chem. Abs.*, 1930, **24**, 129.

[10] French Patent 637,050, 1926; *Brit. Chem. Abs.* **B**, 1930, 360.

The production of olefins from liquid or solid hydrocarbons is accomplished by heating a mixture of the vapors of such hydrocarbons with a gas containing at least 50 per cent oxygen, and in proportions which are insufficient for complete oxidation, to temperatures of 650° to 900° C. Water, either in the form of liquid or vapor, may be added to the gaseous mixture. This process is applicable to such substances as tars, petroleum residues and bitumen.[12] The gases so obtained are rich in olefins which can be used in the preparation of glycols and higher alcohols (see Chapter 22). Conversion of these gases to benzene can be effected with contact agents such as pumice, heavy metals, carbonates and other salts of the alkaline earth metals (see Chapter 5).

In dehydrogenating gaseous hydrocarbons, Hopkins [13] causes the gases to pass through a heated tube into which air or oxygen is fed at regular intervals. The temperature maintained during the process varied from 250° C. for gases of high molecular weight to 470° C. for those of lower molecular weight. For the dehydrogenation of natural gas or the vapors of petroleum distillates a series of reaction zones kept at progressively higher temperatures is recommended. Ramage,[14] on the other hand, suggests the use of reducible metallic oxides, such as ferric oxide, at temperatures of about 550° C.

OXIDATION OF ETHYLENE HYDROCARBONS

The oxidation of ethylene to formaldehyde was reported by Schützenberger,[15] who obtained the solid polymer (trioxymethylene) by conducting a mixture of ethylene and oxygen through a glass tube heated to 400° C. Bone and Wheeler [16] from a study of the slow oxidation of ethylene, at 250° to 400° C. under pressures of 1¾ to 2⅓ atmospheres or at 300° to 500° C. under reduced pressure, also observed the formation of formaldehyde. Later, however, Willstätter and Bommer [17] showed that by working at higher temperatures (545° to 600° C.) larger yields of formaldehyde could be obtained, though it was necessary to dilute the reacting gases with nitrogen. They also found that catalysts accelerated the oxidation of ethylene but were unable to detect any formaldehyde under these conditions. With an osmium catalyst oxidation of ethylene (with oxygen) began at 130° C., but with copper a somewhat higher temperature (250° C.) was required.

The slow oxidation of ethylene was studied by Blair and Wheeler [18] and their conclusions were in general agreement with those reached by Willstätter and Bommer. In these experiments, Blair and Wheeler passed gaseous mixtures of ethylene and oxygen diluted with nitrogen (usually about 60 to 65 per cent of the mixture) through a circulation apparatus for periods of time varying from 12 to 50 hours. The temperatures ranged from 560° to 575° C., and the time of contact for the gases in the reaction zone varied from 1 to 4 seconds. The best result, 75 per cent of the reacting ethylene converted to formaldehyde, was obtained under the following conditions: temperature, 575° C.; circulation

[11] Soc. d'études et d'exploitation des matières organiques, British Patent 282,690, 1927; *Chem. Abs.*, 1928, 22, 3667.
[12] I. G. Farbenindustrie A.-G., British Patent 267,155, 1926; addn. to British Patent 265,234, 1926; *Chem. Abs.*, 1928, 22, 1164.
[13] U. S. Patent 1,808,168, June 2, 1931; assigned to Standard Oil Development Co.
[14] U. S. Patent 1,678,078, July 24, 1928; assigned to Bostaph Engineering Co.; *Chem. Abs.*, 1928, 22, 3418.
[15] *Bull. soc. chim.*, 1879, 31, 482; *Chem. Zentr.*, 1879, 484.
[16] *J.C.S.*, 1903, 83, 1074.
[17] *Ann.*, 1920, 422, 36; *Chem. Abs.*, 1921, 15, 1295.
[18] *J.S.C.I.*, 1922, 41, 303T. Also, *J.S.C.I.*, 1923, 42, 415T.

period, 40 hours; and time of contact, 1 second. In addition to formaldehyde they obtained appreciable quantities of both acetaldehyde and formic acid. A short heating period is necessary for the production of both these substances, since acetaldehyde is an early intermediate product and formic acid is unstable. A slight excess of oxygen in the gaseous mixture favors a larger yield of formic acid, whereas a slight deficiency or a large excess assists in the formation of acetaldehyde. The presence of steam tends to stabilize the formaldehyde (another intermediate product) and prevent its immediate oxidation. Ammonia, however, exhibits a much stronger stabilizing effect.

Blair and Wheeler further observed, using an apparatus similar to that of Willstätter and Bommer, that formaldehyde was not produced when the diluted mixture of ethylene and oxygen was passed once at 405° to 540° C. through a heated tube containing a platinum or ferric oxide catalyst, unless the time of contact was extremely short (less than 0.0001 second). Even then the quantity of formaldehyde was very small. They therefore concluded that the catalyst lowers the temperature at which the various oxidation reactions take place and makes them follow one another at very short intervals.

In the light of Bone's hydroxylation theory, the oxidation of ethylene can be represented as follows:

$$\begin{aligned} C_2H_4 \longrightarrow CH_2{:}CHOH \longrightarrow CH_3CHO &\longrightarrow CH_2(OH)CHO \\ &\longrightarrow HCHO \longrightarrow HCOOH \longrightarrow CO_2 + H_2O \end{aligned}$$

Continuing their work Wheeler and Blair [19] investigated the oxidation of mixtures of methane and ethylene in the presence of some of the oxidation products. The gas used was coal gas, which contained both methane and ethylene together with two of their oxidation products, namely hydrogen and carbon monoxide. The temperatures employed varied from 400° to 720° C. and the times of contact in the reaction chamber, from 0.8 to 2.4 seconds. As in their previous experiments, the mixtures of coal gas and oxygen were diluted with nitrogen.

The rate of oxidation of the hydrocarbons was not greatly affected by the presence of the intermediate oxidation products. The yield of formaldehyde was slightly less than that obtained from methane alone. With increasing temperatures first one constituent and then another begins to react, and the rates of reaction increase rapidly until they attain a constant ratio to one another. A comparison of these rates shows that carbon monoxide and water are the chief products of the slow-oxidation of methane under conditions which decompose formaldehyde. At these temperatures and times of contact hydrogen is oxidized first, then methane, and finally carbon monoxide. The rapid increase in the rate of oxidation of carbon monoxide with rising temperature explains the presence of carbon dioxide among the oxidation products at high temperatures.

The influence of contact agents was also investigated. It was observed that at low temperatures the oxidation and decomposition of the intermediate products were accelerated in the presence of pumic to a greater degree than that of the hydrocarbons. At higher temperatures, however, the oxidation of the hydrocarbon increased and there was an accumulation of hydrogen and carbon monoxide. Ferric oxide has a similar effect, but, in addition, accelerated the decomposition of formaldehyde. The catalytic effect of mercury was found to be small; the rate of oxidation of ethylene, carbon monoxide and hydrogen was accelerated somewhat, but the rate of oxidation of methane was hardly affected. With mercury the yield of formaldehyde was greater than that obtained when either pumice or ferric oxide was employed as the catalyst.

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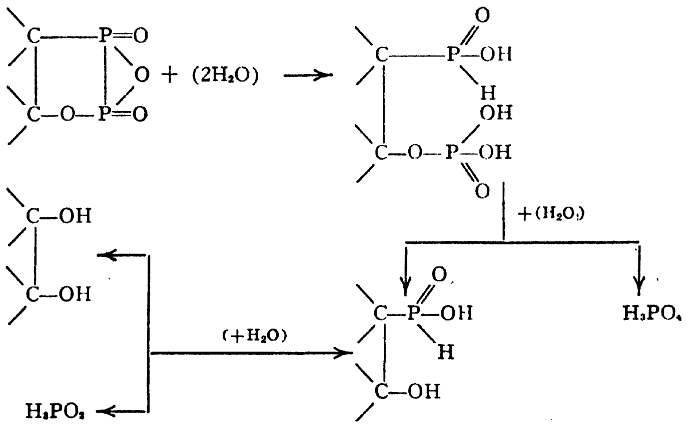
[19] *J.S.C.I.*, 1923, 42, 260T.

When coal gas, without the addition of oxygen, was passed over ferric oxide at 410° C. the carbon monoxide and hydrogen were oxidized while the hydrocarbons were unattacked. It was suggested, therefore, that this be made the basis of a partial combustion method of gas analysis in which the carbon monoxide and hydrogen are first burned by ferric oxide, and the methane is then determined in the usual manner.

Inasmuch as one of the effects of a catalyst is to lower the temperature at which reaction between ethylene and oxygen takes place, Reyerson and Swearingen[20] investigated the use of metallized silica gels. They expected such catalysts to so lower the temperature of reaction that the partial oxidation of ethylene could be effected and a mechanism for its oxidation ascertained. The gels were metallized with gold, silver, platinum, palladium and copper, and the working temperatures ranged from 100° to 300° C. Mixtures of ethylene, oxygen and nitrogen were used and in no instance did the sum of the ethylene and oxygen volumes exceed 50 per cent of the total gas volume. The rates of flow of the gaseous mixtures were varied over wide ranges. Only water and carbon dioxide were produced and aldehydes could not be detected. The catalysts, however were effective with ethylene at lower temperatures than were reported with methane (see Chapter 37). The copper, platinum and palladium began to be effective at 100° C. Silver was the least effective catalyst.

Willstätter and Sonnenfeld[21] tried sulphur as a catalyst and found it inactive at room temperature, while phosphorus was active, but reacted with the olefins yielding compounds of a new type, olefinphosphorous oxides. For instance, if the reaction between one molecule of cyclohexene and two atoms of phosphorus is interrupted after three atoms of oxygen have been absorbed, the product is a yellow, hygroscopic powder, having the formula $C_6H_{10}P_2O_3$. It is known as a phosphorite and is more unstable than the final product obtained by allowing the reaction to be completed. The end result is a phosphorate of the formula $C_6H_{10}P_2O_4$. The phosphorates are very hygroscopic, snow-white to faintly yellowish crystals, and have a violent reaction with water, hydrolyzing to an acid ester. On further hydrolysis, phosphenylous acid and phosphoric acid are formed along with phosphinic acid and an alcohol. The reaction may be indicated in the following manner:



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[20] *J.A.C.S.*, 1928, 50, 2872.
[21] *Ber.*, 1914, 47, 2801.

In a process of Mittasch, Willfroth and Balz,[22] a mixture of ethylene and oxygen is passed over a catalyst consisting of burnt clay or diatomaceous earth impregnated with boric or phosphoric acid. The reaction temperature is 375° C. Bibb,[23] on the other hand, used oxides of nitrogen as catalysts for the oxidation of ethylene to formaldehyde with air.

The slow or incomplete oxidation of ethylene can also result in the formation of unsaturated hydrocarbons of high molecular weight. Thus, Weinmann[24] observed when ethylene is suddenly heated with insufficient oxygen for complete combustion (particularly moist oxygen) to a temperature corresponding to red heat and then rapidly cooled, the condensate contains unsaturated hydrocarbons other than ethylene. On distillation the condensate yielded one fraction, boiling about —7° C., which contained a mixture of butadiene and ethylethylene. Another fraction, boiling about 80° C., proved to be a mixture of hexene and hexane. The former can be used for welding and as an aviation fuel.

Glycol is also obtained from ethylene by the action of air and water under pressure, using arsenic, antimony, gold, copper, iron, or compounds or mixtures of these metals as catalysts.[25] A temperature of 150° to 300° C. is employed.

Cyclic glycols are prepared by treating unsaturated cyclic compounds with hydrogen peroxide in the presence of acids or of easily hydrolyzed salts.[26]

Ethylene oxide has been made by heating equimolecular quantities of ethylene and oxygen in the vapor phase under pressure.[27] Formation of acetaldehyde is suppressed by controlling the temperature of reaction. Acetaldehyde may be produced by the use of hydration catalysts such as zinc chloride or phosphoric acid. Likewise acetic acid can be formed by using an excess of oxygen at high temperatures and silver, copper, or metallic oxides as catalysts.

Schultze[28] studied the effect of oxygen on unsaturated hydrocarbons in the presence of bromine. If ethylene, propylene or butylene were absorbed by bromine water in the presence of pure oxygen, more of the gaseous mixture was absorbed than corresponded to the quantity of hydrocarbon present. Obviously some oxygen was also absorbed. This was not accounted for by the solubility of oxygen in bromine water, for similar results were obtained when the latter was presaturated. Therefore a bromine-sensitized oxidation of the hydrocarbons to carbon dioxide and water was suspected. On analysis of the solution carbon dioxide was found to be present. This proved that some oxygen had been used to oxidize the hydrocarbons.

Riley and Friend[29] investigated oxidation with selenium dioxide. When gaseous ethylene was passed over selenium dioxide at temperatures between 50° and 300° C. glyoxal was formed. It was isolated either as glyoxal ($CHO{\cdot}CHO$) or as a solid polymer ($(CHO{\cdot}CHO)_n$). The reaction may be indicated as

$$2CH_2{=}CH_2 + 3SeO_2 \longrightarrow 2(CHO)_2 + 3Se + H_2O$$

At 110° to 120° C. the reaction is only about 33 per cent complete due to the coating of selenium on the selenium dioxide; at 220° to 240° C. the unreduced selenium dioxide sublimed through the molten selenium, and reacted with ethylene giving an 82.4 per cent yield of glyoxal. The carbon dioxide formed probably accounts for the remainder of the ethylene.

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[22] U. S. Patent 1,487,020, March 18, 1924; assigned to Badische Anilin- und Soda-Fabrik; *Chem. Abs.*, 1924, **18**, 1672.

[23] Canadian Patent 302,672, 1930; *Chem. Abs.*, 1930, **24**, 4519.

[24] German Patent 402,993, 1921; *J.S.C.I.*, 1925, **44**, 229B.

[25] Soc. française de catalyse généralisée, French Patent 729,952, 1931; *Chem. Abs.*, 1933, **27**, 312; French Patent 41,474, 1931; addition to 729,952; *Chem. Abs.*, 1933, **27**, 2697; French Patent 41,810, 1933; addition to 729,952; *Chem. Abs.*, 1933, **27**, 4546; Dreyfus, British Patent 387,372, 1933; *Chem. Abs.*, 1933, **27**, 4540.

[26] Meerwein, Schoeller, Schwenk and Borgwardt, German Patent 574,838, 1933; assigned to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1933, **27**, 4540.

[27] Dreyfus, French Patent 744,401, 1933; *Chem. Abs.*, 1933, **27**, 3942.

[28] *J.A.C.S.*, 1931, **53**, 3561.

[29] *J.C.S.*, 1932, 2342; *J.S.C.I.*, 1932, **51**, 518. Riley, British Patent 376,306, 1931; *Brit. Chem. Abs.* **B**, 1932, 973; French Patent 734,537, 1932; *Chem. Abs.*, 1933, **27**, 999; German Patent 574,162, 1933; *Chem. Abs.*, 1933, **27**, 3486; all patents assigned to Imperial Chemical Industries, Ltd.

At temperatures of about 150° C. and under pressure, ethylene is oxidized by solutions of oxidizing agents (e.g., 40 per cent sulphuric acid containing chromic acid) to acetic acid or its esters.[30]

The oxidation of isoprene with perbenzoic acid yields β-methyl-butadiene αβ-oxide, an oxide containing a double bond.[31] It is violently isomerized by mineral acids to tiglaldehyde.

MECHANISM OF THE OXIDATION OF OLEFINS

As already mentioned, Blair and Wheeler[32] concluded that the oxidation of unsaturated hydrocarbons took place in steps which were in accord with the hydroxylation theory.

Thompson and Hinshelwood,[33] from their work on the rate of reaction of oxygen with ethylene at temperatures between 400° and 500° C., believed that the reaction progressed by a chain mechanism. It was suggested that the first stage was the formation of an unstable peroxide, $C_2H_4:O_2$. When one molecule of this peroxide collides with an ethylene molecule, two hydroxylated molecules, e.g., $CH_2:CHOH$, are produced and these continue the chain. If, however, the peroxide collides with an oxygen molecule, then it is either decomposed or oxidized to stable products. The reaction is greatly retarded by an increase in the surface of the vessel exposed to the gases. Furthermore, a consideration of the temperature coefficient and the influence of foreign gases on the velocity of reaction indicates that the reaction chains are not of great length. Spence and Taylor[34] studied the reaction of ethylene with oxygen and with ozonized oxygen at temperature between 260° and 440° C. They found that the extent of total reaction is greatly increased by the presence of small quantities of ozone and concluded, therefore, that ozone is an initiator of reaction chains of short lengths.

The slow combustion of ethylene has also been investigated by Lenher, using both long times of contact in a single-pass system[35] and short times of contact in a circulatory system.[36] When the first method was employed the products were carbon monoxide and dioxide and hydrogen, and the condensible products contained ethylene oxide, ethylene glycol, glyoxal, formaldehyde, formic acid and water. Raising the temperature increased the yields of the various substances. Above 400° C., however, the proportion of condensate began to decrease on account of secondary reactions. Increasing the time of contact also increased the yields. The rate of reaction was proportional to the third power of the ethylene concentration.[37] On the other hand, increasing the surface in contact with the gases reduced the reaction velocity. In fact, the reaction was entirely inhibited in a packed vessel below a temperature of 450° C. These last two phenomena are characteristic of chain reactions. The lining of the reaction vessel also influenced the course of the reaction. Oxides of nitrogen were found to react directly with ethylene and, therefore, could not be considered as catalysts.[38]

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[30] I. G. Farbenindustrie A.-G., French Patent 743,342, 1933; *Chem. Abs.*, 1933, **27**, 3721.

[31] Pummerer and Reindel, *Ber.*, 1933, **66B**, 355; *Brit. Chem. Abs.* **A**, 1933, 373.

[32] *Loc. cit.*

[33] *Proc. Roy. Soc. (London)*, 1929, **A125**, 277; *Brit. Chem. Abs.* **A**, 1929, 1243; *Chem. Abs.*, 1929, **23**, 5394.

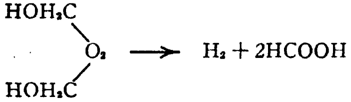
[34] *J.A.C.S.*, 1930, **52**, 2399.

[35] *J.A.C.S.*, 1931, **53**, 3737. See also, *J.A.C.S.*, 1931, **53**, 2420. Compare Spence, *Nature*, 1931, **128**, 873; *Chem. Abs.*, 1932, **26**, 1572.

[36] *J.A.C.S.*, 1931, **53**, 3752.

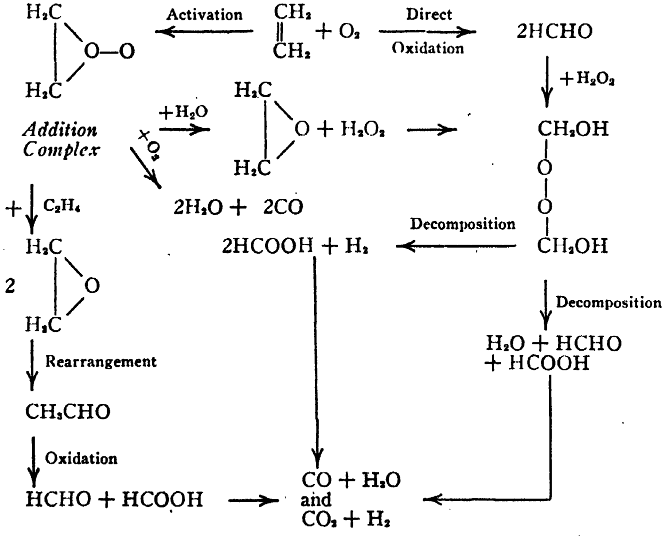
[37] Thompson and Hinshelwood (*loc. cit.*) also observed that the rate of reaction was proportional to the third power of the ethylene concentration.

Similar results were obtained in a much larger reaction vessel except that dioxymethyl peroxide, $(HOCH_2)_2O_2$, was the principal product in the condensate. Other products obtained at the same time were formaldehyde, formic acid, ethylene oxide, the oxides of carbon, and hydrogen. In silica vessels the formation of dioxymethyl peroxide was greatly reduced, and entirely suppressed in iron or aluminum vessels coated with potassium chloride or silicate. Decreasing the formation of this substance resulted in an increased yield of formaldehyde. The formic acid obtained in these experiments apparently came from the dioxymethyl peroxide, as this compound decomposes to yield hydrogen and formic acid.



The experiments in the circulatory system were conducted between temperatures of 410° and 600° C. with short times of contact, usually about 3 seconds. The principal products of the reaction were ethylene oxide and formaldehyde. Other products, such as dioxymethyl peroxide, acetaldehyde, formic acid, oxides of carbon and water, were formed in varying quantities. At temperatures above 450° C. the polymerization of ethylene to higher monolefins becomes an important reaction, the principal polymerization products being propylene and a small quantity of butylene.

Lenher represented the possible mechanism of the oxidation of ethylene as follows:



According to Lenher, the reaction of ethylene with oxygen appears to take place in two ways: either by the direct oxidation of ethylene to formaldehyde, or by the formation of an addition complex or peroxide which in turn yields ethylene oxide. The early appearance of both formaldehyde and ethylene oxide as intermediate oxidation products is evidence that the formation of these two substances is the primary step in the oxidation of ethylene. Hydrogen peroxide is also formed during the reaction and probably reacts with formaldehyde to form dioxymethyl peroxide.

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[38] *Cf.* Bibb, *loc. cit.*

The effect of oxygen on propylene at high propylene and low oxygen concentrations was investigated by Lenher.[39] The time of contact varied from 3 to 18 seconds and the temperature from 500° to 600° C. In addition to oxidation, pyrolysis takes place due to the activation of the propylene by oxygen. The oxidation products were acetaldehyde, formaldehyde, formic acid, carbon oxides and water.

The primary reaction products of pyrolysis were higher monolefins; butylenes, amylenes, and hexylenes. Secondary products were olefins, paraffins and hydrogen. Comparison of results, both in the presence and absence of oxygen, showed that the temperature at which pyrolysis is appreciable, is lowered greatly by the presence of small amounts of oxygen, and the rate is quite markedly increased.

Riley and Friend reported that oxidation of propylene with selenium dioxide gave a 19 per cent yield of methyl glyoxal.[40]

The formation of peroxides as one of the intermediate oxidation products was also demonstrated by Lewis[41] in a study of the low-temperature oxidation of amylene. The variations of pressure with temperature of mixtures of amylene and oxygen were observed. The pressure-temperature curves showed three distinct sections which were accounted for as follows: (1) a region up to 220° to 230° C., which deviates but slightly from the vapor pressure curve and indicates very little reaction; followed by (2) a region of vigorous reaction (up to 237° to 241° C.), which is characterized by a decrease in pressure to a minimum; (3) and a region of rapid increase in pressure, attributed to the oxidation of the products formed in the second stage. Analysis of the gases during the first stage gave evidence of the formation of oxides of carbon and aldehydes. Lewis, therefore, suggested that peroxides are formed and decompose to yield aldehydes during the first stage. Increasing the temperature increases the rates of formation, decomposition and polymerization of the aldehydes, hence the drop in pressure during the second stage. After the minimum pressure is reached sufficient unstable material is present to set up chain reactions giving rapid oxidation. Catalysts, such as pumice or charcoal, accelerate oxidation. Inhibitors, such as lead tetraethyl, almost eliminate the contraction part of the curve. These observations also suggest that the second step in the combustion of a paraffin hydrocarbon is the oxidation of a primarily formed unsaturated compound to a readily decomposed peroxide. The energy of decomposition of the peroxide assists the further oxidation of the aldehyde formed during its decomposition.

The mechanism proposed by Reyerson and Swearingen[42] accounts for the oxidation of ethylene in the presence of metallized silica gels as the result of collisions of the ethylene molecules with oxygen molecules which have been adsorbed and activated by the effective catalyst centers. On the other hand, the collision of oxygen molecules with adsorbed ethylene molecules was ineffective.

[39] *J.A.C.S.*, 1932, 54, 1830.
[40] *J.C.S.*, 1932, 2342.
[41] *J.C.S.*, 1929, 759.
[42] *Loc. cit.*

RELATIVE RATES OF OXIDATION OF OLEFINS

In determining the relative rates of oxidation of olefins Davis[43] exploded various ethylene-propylene and ethylene-isobutylene mixtures with oxygen and analyzed the gases before and after reaction. In every instance combustion was incomplete, that is, both olefins and oxygen were found in the reaction products. The analyses, however, indicated that both propylene and isobutylene burned faster than ethylene.

Mixtures of ethylene and isobutylene were also dissolved in water and oxidized by slowly adding a saturated solution of permanganate. The quantity of reagent added was not sufficient for complete oxidation and the proportion of each olefin unoxidized was determined by boiling out the gases and analyzing them. The relative rates of reaction of the olefins in these two series of oxidations were calculated using the formula developed by Francis, Hill and Johnston:[44]

$$\frac{K_A}{K_B} = \frac{\log(1 - r_A)}{\log(1 - r_B)}$$

where r_A and r_B = fractions of olefins A and B which react; and
K_A and K_B = velocity constants of oxidation reactions of the two olefins.

From the data obtained in the combustion with oxygen the following ratios were derived:

$$\frac{K \text{ propylene}}{K \text{ ethylene}} = 1.71 \quad \text{and} \quad \frac{K \text{ isobutylene}}{K \text{ ethylene}} = 2.8$$

from which it is apparent that the relative rates of combustion with oxygen are

Ethylene	1
Propylene	1.7
Isobutylene	2.8

Similarly, it was found that for oxidation with aqueous permanganate $\frac{K \text{ isobutylene}}{K \text{ ethylene}} = 1.64$; or the relative rates of oxidation with permanganate for ethylene and isobutylene may be represented by 1 and 1.6, respectively.

This greater reactivity of the higher molecular weight olefins with oxygen is somewhat analogous to their reaction with sulphuric acid. As pointed out in Chapter 16, the maximum reactivity with sulphuric acid is shown with olefins containing 6 or 7 carbon atoms.

Howes and Nash[45] studied the oxidation with potassium permanganate of pentene-2, trimethylethylene, cyclohexene, methyldiethylethylene, diisobutylene (2,4,4-trimethylpentene-2) and diamylene (2,3,4,4-tetramethylhexene-2) dissolved in n-hexane. Five per cent solutions of the hydrocarbons were prepared and agitated with 2 per cent alkaline permanganate solution for 6 hours at 0° C. Samples were withdrawn from time to time and the bromine values determined. The results indicated that the pentene, cyclohexene and trimethylethylene were easily oxidized, reaction being complete in 5 hours. Diisobutylene and diamylene, on the other hand, were surprisingly stable. It was further observed that reaction was more rapid when alkaline permanganate was employed than with neutral permanganate.

Unsaturated hydrocarbons could not be removed quantitatively from cracked gasoline with permanganate. Howes and Nash reported that at 0° C. only a small proportion of these hydrocarbons reacted with permanganate (as indicated by the change in bromine number), and at higher temperatures (room temperature) some aromatics were oxidized. The difficulty of removal not only increases with the molecular weight of the olefin but also with its molecular configuration.

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[43] *Ind. Eng. Chem.*, 1928, **20**, 1055.
[44] *J.A.C.S.*, 1925, **47**, 2222.
[45] *J.S.C.I.*, 1930, **49**, 113T.

AUTOXIDATION OF OLEFINS

One of the characteristic reactions of olefins is that of autoxidation. As has been mentioned, this reaction is especially important in the case of cracked gasolines since it, no doubt, ultimately results in the formation of gum (see Chapter 40).

Hyman and Wagner[46] have shown that hydrogen chloride, stearic acid, and cobalt stearate catalyze the reaction. Acetic acid was almost inert, and triethylamine exerted a negative effect. Their work has shown that for a homologous series the structure of the olefin greatly affects its rate of autoxidation. Generally, olefins with a terminal double bond react less readily than those with an internal double bond. This can be easily seen from the following results obtained with the amylenes. The hydrocarbons were saturated with oxygen, and a catalyst (0.0424 gram of cobalt stearate per 100 cc. of olefin) was added. The samples were kept in ice water and the rate of autoxidation measured after various periods. One cc. of the olefin was added to an alcoholic solution of potassium iodide, and the liberated iodine was titrated with thiosulphate solution.

	Cc. of 0.01*N* $Na_2S_2O_3$ Used After					
	13 Hrs.	19 Hrs.	36 Hrs.	84 Hrs.	156 Hrs.	252 Hrs.
n-Propylethylene	0.00	0.00	0.00	0.00	0.00	—
Isopropylethylene	0.00	0.00	2.90	11.60	23.15	—
unsym.-Methylethylethylene	0.00	0.00	0.00	0.00	0.00	0.00
sym.-Methylethylethylene	1.65	2.85	3.75	7.70	18.00	15.10
Trimethylethylene	1.65	3.00	4.80	8.80	19.75	16.90

Both n-propylethylene and unsym-methylethylethylene which contain terminal double bonds did not undergo autoxidation. On the other hand, sym-methylethylethylene and trimethylethylene, both of which possess an internal double bond, suffered rapid autoxidation. The unusually long induction period for isopropylethylene may possibly have been caused by extensive purification received just prior to use.

These same workers also observed that cobaltic soaps were much more active catalysts than cobaltous soaps. They therefore concluded that, when a cobalt soap acts as a catalyst, the active agent is the oxidized soap.

Bodendorf[47] stated that substances containing two conjugated ethylenic linkages are oxidized by oxygen (in the absence of a catalyst) much more rapidly than compounds containing only one such linkage. The reaction is autocatalytic and results in the formation of multimolecular peroxides which do not show the full normal reactivity of peroxides.

REACTION OF OZONE WITH OLEFINS

It has long been known that olefins react with ozone, though the true character of these reactions was first made clear by Harries.[48] He showed that, in the absence of water, the olefins react with ozone to form thick viscous substances often of an explosive nature. In spite of this characteristic Harries demonstrated that the reaction products contained one ozone molecule for each double bond in the original hydrocarbon.

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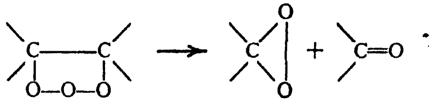
[46] *J.A.C.S.*, 1930, **52**, 4345; *ibid.*, 1931, **53**, 3019.

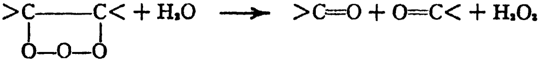
[47] *Arch. Pharm.*, 1933, **271**, 1; *Brit. Chem. Abs.* **A**, 1933, 279.

[48] For a summary of Harries' work, see *Ann.*, 1905, **343**, 311; 1910, **374**, 288; 1912, **390**, 236; 1915, **410**, 1. See also Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, 1922, 137.

Ozonides, or their solutions in absolute alcohol or glacial acetic acid or other solvents, can be decomposed by warming, to yield ketones or aldehydes and peroxides, as follows:



The ozonides also react with water to form hydrogen peroxide and aldehydes or ketones, thus effecting a rupture of the original hydrocarbon at the double bond.



$$\underset{\text{O—O—O}}{>\text{C——C}<} + \text{H}_2\text{O} \longrightarrow >\text{C=O} + \text{O=C}< + \text{H}_2\text{O}_2$$

This hydrolysis of the ozonide, therefore, supplies a method for the preparation of aldehydes and ketones from unsaturated compounds. Since hydrolysis results in a rupture of the original hydrocarbon at the double bond, the identification of the products of hydrolysis often affords a clue to the structure of the unsaturated hydrocarbon.

Blair and Wheeler[49] investigated the production of formaldehyde by the action of ozone on ethylene. They effected the reaction (1) by passing a mixture of air and ethylene (about 3 per cent of the latter) through an ozonizer and (2) by the direct action of ozonized oxygen or air on ethylene. Both of these reactions were carried out in the presence and in the absence of both water and ammonia.

In dilute mixtures the ozone and ethylene combined at ordinary temperatures to form the ethylene ozonide, $C_2H_4O_3$. In the absence of moisture the ozonide decomposes to give formic acid, formaldehyde, and other products. On the other hand, in the presence of moisture, hydrolysis takes place with the formation of formaldehyde and hydrogen peroxide. Most of the latter decomposes, though some of it may react with either ozone or formaldehyde. With small concentrations of ozone very little oxidation of formaldehyde was observed. For example, with about 1 cc. of ozone per liter of mixed gases, 90 per cent (of the ozone) reacted to give formaldehyde. The rate of decomposition of the ozonide appeared to be more or less proportional to its concentration. The addition of ammonia to the gases was said to increase somewhat the yield of formaldehyde by reacting with the aldehyde to form hexamethylenetetramine, and thus preventing oxidation of the aldehyde.

By allowing ozonized air or oxygen to react with ethylene in the presence of steam, Carter and Coxe[50] obtained formaldehyde and formic acid in yields of 70 and 15 per cent, respectively. Formaldehyde was recovered as such or was converted to hexamethylenetetramine by the addition of ammonia. This amine can be separated from the reaction products with carbon tetrachloride. Steam is employed to prevent the accumulation of the explosive ethylene ozonide during oxidation.

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[49] *J.S.C.I.*, 1923, 42, 343, 347.

[50] U. S. Patent 1,423,753, July 25, 1922; assigned to S. Karpen and Bros.; *Chem. Abs.*, 1922, 16, 3095.

In another process both glycol and formaldehyde [51] are produced when ethylene is allowed to react with ozonized air or oxygen, and steam or atomized water at a temperature slightly above 100° C. The reacting gases are mixed in towers which are packed with porous material impregnated with either water or a solution of a catalyst. When the catalyst is a concentrated alkaline solution, or a 0.1 to 1.0 per cent solution of potassium permanganate or potassium chlorate, a yield of 50 to 60 per cent of glycol and 15 to 30 per cent of formaldehyde is obtained. In the absence of such catalysts, however, the yield of glycol is only 15 to 20 per cent and that of formaldehyde rises to 70 to 80 per cent. The reaction may be carried out under pressure and in the presence of tungstic and osmic oxides as catalysts.

Ethylene and ozone react, according to Briner and Schnorf,[52] to form a liquid ozonide which is stable at 0° C., becomes a vitreous mass at —80° C., and can be isolated by vacuum distillation as a highly explosive liquid boiling at 20° C. (at 16 to 17 mm. pressure). It is soluble in water in all proportions. Such aqueous solutions decompose slowly at ordinary temperatures, but rapidly at 65° C. In the hydrolysis of the ozonide more formic acid is obtained than formaldehyde, and hydrogen is also evolved. The evolution of hydrogen is caused by the presence of formaldehyde peroxide (dioxymethyl peroxide) which results from the interaction of water, ozone and ethylene.

$$CH_2{=}CH_2 + O_3 + H_2O \longrightarrow (OH{-}CH_2{-}O)_2$$

The water is present either because of incomplete drying or from the oxidation of some ethylene. On decomposition of the peroxide both hydrogen and formic acid are obtained, as previously mentioned. This is the explanation advanced for the preponderance of formic acid among the reaction products of ozone and ethylene.

Ozonation of ethylene can also be accomplished in the presence of water and the products obtained are the same as those mentioned above. When the ozonide is decomposed with sodium acid sulphite, the chief product is formaldehyde, which is isolated as its addition compound with the acid sulphite. Addition of an ammoniacal solution of this ozonide to a solution of ammonium chloride yields hexamethylenetetramine together with a small quantity of ammonium formate and oxygen.

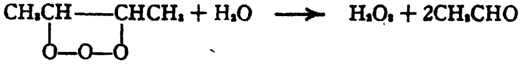
The ozonation of propylene takes place in a very similar manner, and the decomposition products are formaldehyde, acetaldehyde, formic and acetic acids. Peroxides, however, are not formed to as large an extent as from ethylene. This was indicated by a smaller hydrogen evolution during the decomposition of the ozonide of propylene.

All of the three butylenes form ozonides.[53] On hydrolysis, these ozonides can be distinguished from one another by the proportions of acids, aldehydes and acetone formed, as well as by the gas evolved. For example, 2-butylene, when dissolved in methyl chloride and treated with ozone at —80° C., yields a liquid ozonide. Decomposition of this ozonide with water at 70° to 75° C. yields, in addition to acetaldehyde, the principal product, some acetic acid, methane, formic acid, and a small quantity of the oxides of carbon. The principal reaction, therefore, seems to be

[51] Plauson's Forschungsinstitut G.m.b.H., German Patent 344,615, 1920; *J.S.C.I.*, 1922, **41**, 392A.

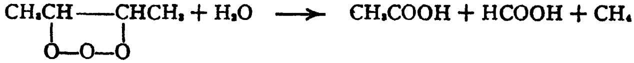
[52] *Helv. Chim. Acta*, 1929, **12**, 154, 181; *Brit. Chem. Abs.* **A**, 1929, 290; *Chem. Abs.*, 1929, **23**, 2149; Swiss Patent 134,937, 1928; *Chem. Abs.*, 1930, **24**, 2471.

[53] Briner and Meier, *Helv. Chim. Acta*, 1929, **12**, 529; *Brit. Chem. Abs.* **A**, 1929, 674.



$$\underset{\text{O—O—O}}{CH_3CH{-}{-}CHCH_3} + H_2O \longrightarrow H_2O_2 + 2CH_3CHO$$

which is accompanied by the side reaction:



$$\underset{\text{O—O—O}}{CH_3CH{-}{-}CHCH_3} + H_2O \longrightarrow CH_3COOH + HCOOH + CH_4$$

This formation of methane appears to be characteristic of the acet-grouping, as methane was also found as one of the decomposition products of propylene ozonide.

The ozonide from isobutylene decomposes rapidly in the absence of water to yield acetone peroxide and formaldehyde. When hydrolyzed with water at 70° C. the same products are obtained together with acetone, formic acid, hydrogen and the oxides of carbon.

The ozonide from 1-butylene which contained 20 per cent of 2-butylene, when hydrolyzed yielded products similar to those obtained from 2-butylene except that hydrogen was obtained instead of methane. These results with isobutylene and 1-butylene indicate that the formation of hydrogen during decomposition of the ozonide is characteristic of the formic grouping.

Although the ozonides just mentioned were made in the presence of inert liquids, it was also observed that the butylenes react with ozone in the gas phase to form non-explosive water-soluble products. These represent intermediate steps in the transformation of the ozonides into their stable end products, aldehydes, acetone and acids. Of the aldehydes and ketones formed, formaldehyde appears to be the most resistant to the action of ozone. The yields of products from the butylenes were somewhat lower than those obtained from ethylene. The maximum yield, based on the ozone, was 72 per cent from isobutylene.

The reactions of the higher molecular weight olefins with ozone are very similar to those already mentioned. They have been used in determining the structures of various compounds. For example, McCubbin and Adkins[54] treated diisobutylene in acetic acid with ozonized oxygen, and then hydrolyzed the ozonides with water and zinc dust. The principal products obtained were acetone, trimethylacetaldehyde and methyl neopentyl ketone. Since the first two products were obtained in practically equivalent quantities, and the quantity of the last named substance was about four times that of either of the other two, it was concluded that diisobutylene is a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, the former being present in the greater quantity. In a similar manner, McCubbin[55] found that triisobutylene is a mixture of three isomeric dodecylenes.

Likewise Whitmore and Church[56] used ozonolysis in the determination of the constitution of diisobutylene. They first fractionated this substance, obtaining two portions (one boiling at 101.2° and another at 104.5° C.) in the ratio of 4 to 1, the lower boiling constituent being present in the greater amount. Ozonolysis of each portion was carried out, the low-boiling constituent giving formaldehyde and methyl neopentyl ketone, as well as a small amount of tertiary butylacetic acid, thus proving it to be 2,4,4-trimethylpentene-1. The high-boiling portion gave acetone, trimethylacetaldehyde and trimethylacetic acid, indicating it to be 2,4,4-trimethylpentene-2. These results agreed with those of McCubbin and Adkins.

[54] *J.A.C.S.*, 1930, **52**, 2547.
[55] *J.A.C.S.*, 1931, **53**, 356. See also Conant and Wheland, *J.A.C.S.*, 1933, **55**, 2499.
[56] *J.A.C.S.*, 1932, **54**, 3710. See *J.A.C.S.*, 1932, **54**, 3706.

Harries and Haeffner[57] obtained amylene ozonide by passing ozone into a dilute solution of the olefin in hexane. Evaporation of the solvent by heating at 60° C. in a vacuum yielded the crude ozonide as a limpid colorless liquid. This crude product was treated with an aqueous solution of sodium bicarbonate. The purified ozonide was analyzed giving values of composition between $C_5H_{10}O_3$ and $C_5H_{10}O_4$.

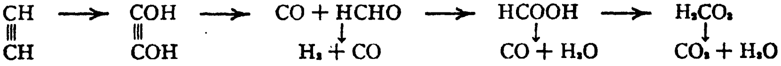
Hexylene ozonide was prepared in the same manner. The crude material was a very viscid liquid, but on distillation gave the normal ozonide as a free-flowing liquid. Distillation was carried out at 60° C. under a pressure of 12 mm. These ozonides were relatively stable, not being readily decomposed by water.

Ozonides of cracked petroleum distillates, derived principally from an olefin mixture of boiling point 125° to 150° C., were suggested by Ramage[58] as substitutes for turpentine and linseed oil.

OXIDATION OF ACETYLENE

Bone and Andrew[59] observed that when oxygen and acetylene are heated in sealed tubes reaction begins at 250° C. and becomes very rapid at 300° C. With a mixture containing equal volumes of oxygen and acetylene or two volumes of acetylene to one of oxygen, explosive combustion[60] occurs at 350° C. With a mixture of two volumes of acetylene to three of oxygen, explosive combustion takes place at 375° C. A relatively large excess of oxygen was found to retard the reaction.

Investigation of the slow combustion of acetylene in a circulatory system indicated that oxidation occurs in a manner similar to that of ethane and ethylene. The main products are formaldehyde, formic acid, water and the oxides of carbon. These products could be accounted for by the hydroxylation theory according to the following transformations:



$$\begin{tikzcd}[column sep=small] \begin{array}{c}CH\\ \vert\vert\vert\\ CH\end{array} \arrow[r] & \begin{array}{c}COH\\ \vert\vert\vert\\ COH\end{array} \arrow[r] & CO + HCHO \arrow[r] \arrow[d] & HCOOH \arrow[r] \arrow[d] & H_2CO_3 \arrow[d] \\ & & H_2 + CO & CO + H_2O & CO_2 + H_2O \end{tikzcd}$$

The reactions, however, are complicated by the fact that, in the presence of a hot catalyzing surface, acetaldehyde is formed from water and acetylene even in the presence of oxygen. This aldehyde then decomposes to methane and carbon monoxide ($CH_3CHO \rightarrow CH_4 + CO$) and competes with the acetylene for the oxygen present, thereby yielding formaldehyde and carbon monoxide:

$$CH_3CHO \longrightarrow CH_2OHCHO \longrightarrow CO + H_2O + HCHO$$

The oxidation of acetylene mixed with oxygen at 250° C. to 315° C. with times of contact of 50 to 200 seconds, has been investigated by Kistiakowsky and Lenher.[61] The condensible reaction products are glyoxal, formaldehyde, formic acid and water. Carbon monoxide and dioxide are the gaseous products. These investigators disagreed with Bone and Andrew, and considered the aldehyde glyoxal (OHC—CHO) the first intermediate oxidation product of acetylene and not the unsaturated alcohol $HOC\equiv COH$. Furthermore they also concluded that glyoxal decomposes to yield carbon monoxide and formaldehyde, ($CHOCHO \rightarrow CO + HCHO$), the formaldehyde being oxidized to formic acid, and this acid in turn being oxidized to carbon dioxide and water. The reaction rates indicate a chain reaction which is homogeneous. In packed reaction vessels, however, the homogeneous oxidation is almost suppressed and a heterogeneous oxidation to carbon monoxide and water takes place on the glass surfaces. The rate of this reaction is roughly proportional to the acetylene and oxygen concentrations. In unpacked reaction vessels the rate is proportional to the square of the acetylene concentration and is slightly retarded by the oxygen concentration. Reaction between acetylene and oxygen was always preceded by an induction period.

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[57] *Ber.*, 1908, 41, 3098; *Chem. Soc. Abs.*, 1908, 94 (1), 846.

[58] U. S. Patent 1,689,599, Oct. 30, 1928; *Brit. Chem. Abs.* B, 1928, 937.

[59] *J.C.S.*, 1905, 87, 1232.

[60] Mondain-Monval and Wellard (*Compt. rend.*, 1933, 196, 1226; *Brit. Chem. Abs.* A, 1933, 694) compare explosive combustion when heating at different rates and constant volume. Various mixtures of acetylene and oxygen (17 to 85 per cent acetylene) will explode at a mean temperature of 310° C., on heating at the rate of 40° C. per minute. At 25° C. per minute the explosive mixture varies from 35 to 70 per cent acetylene content.

[61] *J.A.C.S.*, 1930, 52, 3785.

Oxidation of acetylene in a circulatory system at slightly higher temperature (320° C.) was studied by Spence and Kistiakowsky.[62] The oxidation products were found to be the same as those reported by Kistiakowsky and Lenher. At this temperature the rate of reaction is slightly accelerated or retarded according to whether acetylene or oxygen is in excess. At optimum concentrations the rate of reaction is proportional to the square of the acetylene concentration. With less oxygen present the rate is proportional to a lower power of the acetylene concentration. The presence of nitrogen has very little retarding influence on the reaction rate. An induction period was also observed at this temperature (320° C.) and was considered to be caused by the accumulation of an intermediate product taking part in the chain reaction. It was observed that formaldehyde is oxidized very much faster when mixed with reacting acetylene.

The size of the reaction vessel has an effect on the reaction rate.[63] In vessels smaller than 4 mm. in diameter the reaction took place very slowly, but in vessels greater than 6 mm. in diameter, it proceeded at its normal rapid rate. By coating the surface of a vessel greater than 6 mm. diameter with potassium chloride it was noted that the reaction proceeded at a much slower rate than in a plain glass vessel, indicating that potassium chloride inhibited the reaction.

The catalytic oxidation of acetylene to formaldehyde has been described by Mittasch, Willfroth and Balz.[64] In this process, similar to that used by them for the production of formaldehyde from ethylene, the acetylene and air react at 375° C. in the presence of a catalyst prepared by heating burnt clay or diatomaceous earth impregnated with boric or phosphoric acid.

When acetylene is oxidized in the presence of steam, acetaldehyde and acetic acid are produced. Thus in the process developed by Wohl[65] a gaseous mixture of acetylene, air and steam is passed over a catalyst at 300° to 400° C. and the resulting acetaldehyde and acetic acid are fractionally condensed, or the mixture is completely oxidized to acetic acid. The catalysts used are basic metallic salts (zinc vanadate, molybdate, or chromate dispersed on pumice).

Stuer and Grob[66] described a process in which acetaldehyde is produced from a mixture of acetylene and steam in the presence of metallic oxides at 300° to 500° C. Either atmospheric or increased pressures can be used. Thus, at 400° to 420° C. acetaldehyde is the main product from 1 part of acetylene and 4 parts of steam using bog iron ore as the catalyst. A 50 per cent yield of acetonitrile, together with nitrogenous bases, is obtained by passing equal proportions of acetylene and ammonia over bauxite at 350° to 380° C. Two parts of acetylene and 1 part of hydrogen sulphide passed over specially treated bauxite at 320° C. give almost pure thiophene. Horst and Wietzel[67] use a catalyst such as silicotungstic acid which is free of iron or its compounds.

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[62] *J.A.C.S.*, 1930, **52**, 4837.

[63] Spence, *J.C.S.*, 1932, 686.

[64] U. S. Patent 1,487,020, March 18, 1924; assigned to Badische Anilin- und Soda-Fabrik; *Chem. Abs.*, 1924, **18**, 1672.

[65] British Patent, 154,579, 1920; *Chem. Abs.*, 1924, **15**, 1139.

[66] British Patent 109,983, 1916; assigned to Chem. Fabr. Rhenania; *J.S.C.I.*, 1917, **36**, 1194; *cf.* Soc. Industrielles des Dérivés de l'Acetylene, French Patent 731,309, 1932; *Chem. Abs.*, 1933, **27**, 734.

The production of either acetaldehyde or ethyl alcohol from acetylene should be briefly mentioned again[68] for comparison, although neither is strictly an oxidation of acetylene. The acetylene is first passed into a solution of dilute sulphuric acid which contains a mercury compound as a catalyst. The acetylene combines with water to form acetaldehyde,[69] which can be either oxidized to acetic acid or reduced to ethyl alcohol.[70]

Eberhardt[71] passed a mixture of acetylene, steam and oxygen charged with mercury vapor over compounds of mercury or other heavy metal salts or mixtures of these. For instance, the gases are led over a mixture of active carbon and mercury phosphate. A 60 per cent yield of acetic acid and a 14 per cent yield of acetaldehyde are obtained. A change in the catalyst, such as the use of carbon and aluminum oxide, will alter the proportions of the products formed.

REACTION OF OZONE WITH ACETYLENE

Acetylene and ozone react to form an ozonide which, however, because of its explosive properties, has not been isolated and investigated.[72] An attempt was made to prepare this ozonide by the reaction of acetylene and ozone in the presence of an inert solvent. When the solvent was slowly evaporated the product was a yellow viscous transparent liquid which consisted of about 81 per cent glyoxal and 5.6 per cent formic acid. As carbon dioxide was evolved during this operation there is no doubt but that some acetylene was lost through decomposition of the ozonide. Although the evidence seems to indicate that the ozonide exists temporarily it is an extremely unstable substance. One interesting point, however, is brought out in comparing the reactions of ozone with acetylene and with olefins. In acetylene, the triple bond appears to maintain the linkage of carbon atoms, but with olefins ozonization breaks the double linkage.

OXIDATION OF UNSATURATED HYDROCARBONS IN THE PRESENCE OF NITROGEN OXIDES

Lenher[73] has shown that the reaction between acetylene and oxygen between the temperatures of 170° and 250° C. is catalyzed by the presence of nitrogen peroxide. The acetylene is oxidized, and nitrogen peroxide forms nitric oxide which is oxidized by the oxygen again to nitrogen peroxide. The main reaction product found by Lenher was trimeric glyoxal, yields of 50 per cent or more being obtained. The occurrence of large quantities of carbon monoxide and of only traces of formaldehyde, formic acid and hydrogen seem to indicate that the thermal decomposition of glyoxal to carbon monoxide and formaldehyde is the principal source of this oxide of carbon. The formaldehyde is then either oxidized to formic acid, which in turn decomposes to carbon monoxide and water, or it is oxidized by the nitrogen peroxide to carbon monoxide and water. The course of the oxidation reactions can be indicated as follows:

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[67] U. S. Patent 1,856,639, May 3, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3521.

[68] Consortium für elektrochemische Industrie, British Patent 16,957; 1914; *Chem. Abs.*, 1916, **10**, 253. See also Matheson, British Patent, 132,557, 1918; *Chem. Abs.*, 1920, **14**, 288. Hibbert, *Chem. Met. Eng.*, 1918, **19**, 397.

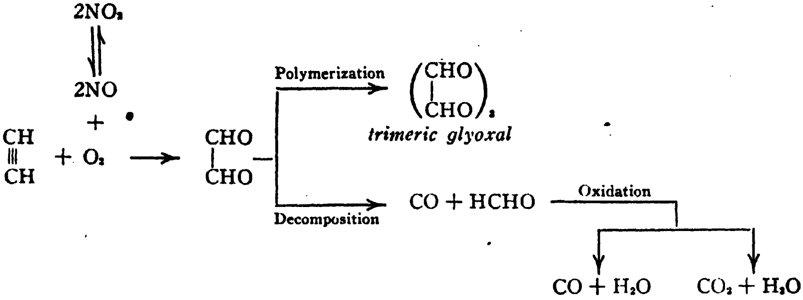
[69] This has been previously discussed in Chapters 28 and 38.

[70] Anon., *Ind. chim. min. met.; Gior. farm. Chim.*, 1917, **66**, 315; *Chem. Abs.*, 1918, **12**, 1386; see Chapters 28 and 38.

[71] German Patent 544,691, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 3521.

[72] Briner and Wunenburger, *Helv. Chim. Acta*, 1929, **12**, 786; *Chem. Abs.*, 1929, **23**, 5156.

[73] *J.A.C.S.*, 1931, **53**, 2962.



In the formation of acetic acid and acetaldehyde using nitrogen oxides as a catalyst, better results are obtained if the mixture is diluted with carbon dioxide.[74]

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[74] Gutehoffnungshütte Oberhausen A.-G., French Patent 720,683, 1931; *Chem. Abs.*, 1932, 26, 3807.

Chapter 40

Autoxidation of Petroleum Distillates. Gum Formation

By autoxidation or spontaneous oxidation is meant, according to Moureu, Dufraisse and Chaux,[1] the combination of the whole molecule of oxygen with an oxidizable substance to form a primary peroxide which may then change in a number of ways to yield stable oxidation products. The theory proposed by these investigators assumes that autoxidation starts with the union of an oxygen molecule, O_2, with a molecule of an autoxidizable substance, A, to yield the peroxide, $[AO_2]$. Such peroxides are formed with the absorption of energy and may then decompose to yield various products or react with other molecules of the autoxidizable substance. It is suggested also that antioxygens or antioxidants catalyze the reverse action, the destruction of these peroxides. Antidetonants or knock suppressors likewise inhibit the formation of peroxides whose explosive properties allow them to act as detonating agents (see also Chapter 44).

Substances which undergo autoxidation include phosphorus and sulphur compounds, sodium sulphite, benzaldehyde, paraffin, petroleum distillates, rubber, turpentine, spermaceti, silk, living tissues, and many other substances.

The oxidation of turpentine or pinene by air is similar to the behavior of olefins and of petroleum distillates containing unsaturated compounds. A brief survey, therefore, of the oxidation of this substance, together with that of some of the cycloparaffins, is of interest. The slow oxidation of pinene results in the formation of peroxides, carbon dioxide, water, organic acids, alcohols, aldehydes, ketones and resinous bodies.[2]

Oxygen is readily absorbed by turpentine oil (which contains pinenes) to yield molecular oxygen compounds (peroxides). On mixing this oxidized oil with indigo the latter rapidly becomes decolorized as a result of oxidation. In fact it seems that one of the characteristic properties of such peroxides is the ease with which half of their oxygen is taken up by substances which are otherwise oxidized with difficulty. Other compounds which exhibit this same behavior towards oxygen are amylene, hexylene, trimethylethylene, some of the fulvenes, ketenes, and unsaturated naphthenes.[3]

In studying the autoxidation of pinene by oxygen Dupont and Crouzet[4] employed two methods: (1) measuring the decrease in the oxygen pressure in the reaction flask by the rise of mercury in a narrow manometer connected to the apparatus (the constant volume method); and (2) measuring the decrease in oxygen volume as indicated by the rise of the meniscus in a eudiometer (the constant pressure method). In diffused light the rate of absorption of oxygen is proportional to the time. The rate of absorption, however, is greatly affected by the intensity of the light and the temperature. For example, when the reaction flask was covered with black paper no oxidation took place for 1200 hours. At the end of that time the rate of oxidation increased very rapidly until it reached the corresponding rate of oxidation in the presence of diffused light. At 80° C. the rate was 2500 times as great, and at 60° C. it was 130 times as great as it was at 15° C. Carbon dioxide was formed at the higher temperatures.

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[1] *Compt. rend.*, 1927, **184**, 413; *Chem. Abs.*, 1927. **21**, 1914. *Chem. Reviews*, 1926, **3**, 113; *Chem. Abs.*, 1926, **20**, 3374. See also Moureu and Dufraisse, *J.C.S.*, 1925, **127**, 1.

[2] Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, **1922**, 427.

[3] Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, **1**, 513, 514.

[4] *Bull. inst. pin.*, 1929, **55**, 101; *Pure Science*, 1929, **3**, 78; *Chem. Abs.*, 1929, **23**, 3455.

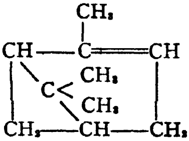
The rate of oxidation also increases in the presence of certain metallic catalysts, such as the resinates of cobalt, iron, lead, chromium and nickel. The first of these was found to be the most active, but after a time its effectiveness diminishes as a result of decomposition.[5] The rate of oxidation is reduced by the presence of hydroquinone, gallic and pyrogallic acids, stannous chloride, reduced copper, copper resinate, sulphur, and other substances.[6]

Some substances act first as antioxidants and then as pro-oxidants. Manganese resinate, for example, when added in the proportion of 1 part to 1000 parts of pinene was found to reduce the rate of oxidation for 100 hours, after which the rate is accelerated several hundred times. When added in the proportion of 1 part to 100 parts of pinene, oxidation did not start for 700 hours.

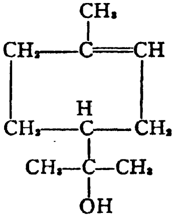
The autoxidation of pinene can be shown also by the spontaneous ignition of cotton on exposure to air after being treated with turpentine to which has been added a heavy metal resinate.[7] When asbestos fiber is substituted for cotton the temperature of the oil rose to 300° C. The spontaneous ignition of cotton can be retarded by phenol, β-naphthol or quinol, and prevented by α-naphthol, aniline, diphenylamine, quinhydrone, and other similar substances, and also by sulphur.

When dissolved in acetic acid and oxidized with aqueous hydrogen peroxide at 50° to 60° C., α-pinene yields principally α-terpineol (partly in the free state and partly as the acetate), small proportions of borneol (as the acetate) and dipentene, a trace of aldehyde of the formula $C_{10}H_{16}O$, a small quantity of trioxyterpan, $C_{10}H_{17}(OH)_3$, and some resinous material.[8] β-Pinene, on the other hand, when oxidized with hydrogen peroxide under the same conditions yields an oily product in which were identified principally borneol and fenchyl alcohol (as acetates).[9]

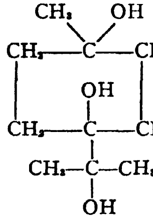
The relation of these substances can be shown by the following formulas:



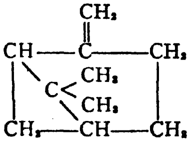
α-pinene



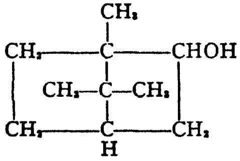
α-terpineol



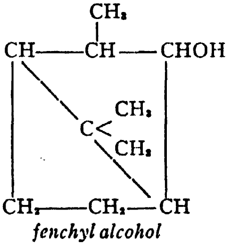
trioxyterpan



β-pinene



borneol



fenchyl alcohol

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[5] Taradoire, *Compt. rend.*, 1926, **182**, 61; *Brit. Chem. Abs.* **B**, 1926, 135.

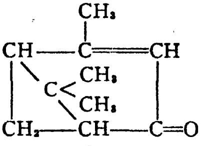
[6] *Cf.* oxidation of oils, Chapter 42.

[7] *Cf.* oxidation of gasoline and lubricating oil discussed later in this chapter.

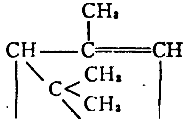
[8] Henderson and Sutherland, *J.C.S.*, 1912, **101**, 2288.

[9] Henderson and Chisholm, *J.C.S.*, 1924, **125**, 107.

When oxidized in acetic anhydride with chromium trioxide, the CH_2 group adjacent to the double bond is converted to a ketone or an alcohol grouping. Thus α-pinene yields verbenol and verbenone.[10] Acetic anhydride is used as a solvent in order to absorb any water formed during the oxidation, and also to acetylate alcohols as formed and thus prevent their further oxidation.



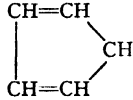
verbenone

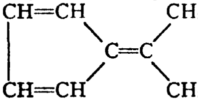


verbenol.

On passing a mixture of turpentine vapor and air through a copper net heated to 400° C., the hydrocarbon is oxidized and the heat of the reaction is sufficient to keep the copper glowing. The products of the reaction are carbon monoxide, carbon dioxide, some ethylene hydrocarbons, about 21 per cent of water-soluble substances, and 60 to 70 per cent of oil. About 75 per cent of the oil distills between 160° and 173° C. and this particular fraction contains a large percentage of cymene.[11] It therefore has a pleasant odor and is suitable for use in perfumery. The presence of steam in the gaseous mixture during oxidation reduces the yield of oil.

Peroxides are formed in some instances when ozone is used. Ramage[12] suggested the production of the terpene peroxide, $C_{10}H_{18}O_2$, by blowing ozonized air through eucalyptus oil at 80° C. After removing the peroxide by a current of air it could be further oxidized to the diperoxide, $C_{10}H_{18}O_4$, with an excess of ozonized air. This diperoxide is a colorless oil which, when placed in contact with water, slowly liberates active oxygen for a long period of time.

Another class of compounds which are easily oxidized and polymerized are cyclopentadiene and its derivatives, the fulvenes. Cyclopentadiene, , can be isolated from the first fractions in the distillation of crude benzene. It polymerizes on standing to the dimer, $C_{10}H_{12}$, which is partially reconverted to the original hydrocarbon on distillation. The dimer takes up oxygen from the air forming the diperoxide.[13]

The fulvenes, which were first prepared by Thiele,[14] are made by condensing ketones (acetone, acetophenone, or benzophenone) with cyclopentadiene. Dimethylfulvene, for example, has the formula  and when dissolved in benzene quickly absorbs oxygen from the air to form a voluminous white precipitate which gradually becomes granular.[15] Light and heat shorten the time required for this reaction. The precipitate is a diperoxide of dimethylfulvene ($C_8H_{10}O_4$), which decomposes with violence when heated to 130° C. It is insoluble in the usual organic solvents, but dissolves, with some decomposition, in hot nitrobenzene and in acetic acid. On standing, it gradually becomes yellow and loses its explosive properties. This peroxide however is a very mild oxidizing agent. Methylphenylfulvene takes up oxygen much more slowly, forming the diperoxide of the formula $C_{18}H_{12}O_4$. Contrasted with these, cyclopentadiene absorbs only a small quantity of oxygen and forms a resinous product.

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[10] Treibs and Schmidt, *Ber.*, 1928, **61B**, 459; *Chem. Abs.*, 1928, **22**, 1969.
[11] Orlov, *Ukrainskii Khem. Zhurnal*, **2**, 1; *Chem. Zentr.*, 1926, **2**, 660; *Chem. Abs.*, 1927, **21**, 3894.
[12] U. S. Patent 1,585,602, May 18, 1926; assigned to Ozonid Corp.; *Brit. Chem. Abs.* **B**, 1926, 610.
[13] Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436; *Chem. Abs.*, 1920, **14**, 1327.
[14] *Ber.*, 1900, **33**, 666.
[15] Engler and Frankenstein, *Ber.*, 1901, **34**, 2933; *J.S.C.I.*, 1901, **20**, 1151.

In diffused sunlight 1,3-dimethylcyclopentane absorbs oxygen even at pressures as low as 60 mm. The product formed is a peroxide which, after reacting with potassium iodide, yields a mixture of 5-methyl-2-hexanone and 4-methyl-2-hexanone. These ketones must have been formed from the peroxide, the initial product of oxidation, by a rupture of the cyclic nucleus.[16]

Cyclopentane is found in certain fractions of some crude oils, and from such oils cyclopentanone (adipic ketone) can be obtained by oxidation. This ketone, according to Mentzel,[17] is very easily condensed with aromatic aldehydes in the presence of alkalies.

Cyclohexene, when kept in contact with oxygen for a long period, yields a small quantity of cyclohexene peroxide.[18] This substance, which is a mobile liquid boiling at 54° to 56° C. at 0.5 mm., possesses a pungent odor and is an energetic oxidizing agent. Molecular weight determinations indicate that the peroxide is monomolecular, but the sirupy residue from the distillation of the peroxide, which has the same composition as the peroxide, is bimolecular. These facts appear to indicate that two molecules of the peroxide combine to form a new substance with peroxide properties. Determination of the active oxygen content of the dimeric form indicates that it contains only one peroxide group.

Zelinsky and Borisov[19] observed that 20 grams of cyclohexene can absorb 3200 cc. of oxygen in 151 days. The rate of absorption is rapid at first, then decreases, and finally ceases altogether. The oxygen absorbed corresponds to about 1 atom of oxygen per molecule of cyclohexene. The unchanged cyclohexene was removed by allowing the mixture to stand for three months in a vacuum desiccator over sulphuric acid. After evaporation, a tough, resinous, reddish yellow mass was obtained which gave the characteristic peroxide tests. Analysis indicated the substance to be cyclohexene peroxide of the formula $C_6H_{10}O_2$.

Cyclohexene, however, is oxidized much more rapidly in the presence of certain metallic catalysts. Willstätter and Sonnenfeld[20] prepared a catalyst for such a reaction by heating osmium ammonium chloride in the presence of hydrogen. When 0.5 gram of the osmium so prepared was added to a solution of 10 grams of cyclohexene dissolved in 10 grams of acetone the mixture absorbed 0.86 moles of oxygen in 22 hours. The products consisted chiefly of 2-cyclohexene-1-ol and 1-cyclopentene-1-aldehyde (1-methylal-1-cyclopentene) and adipic acid together with small proportions of unchanged cyclohexene and 2-hydroxycyclohexanone. No oxidation occurred when the cyclohexene was dissolved in acetic acid. Platinum, palladium, and ruthenium could not be substituted for osmium, and tellurium showed very little catalytic activity. No indication of the intermediate oxidation products (peroxides) was found, which showed that osmium accelerated their decomposition. Oxidation generally proceeds in more than one direction with the formation of secondary and transformation products. Substances which possess acidic properties appear to retard oxidation.

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[16] Chavanne, *Bull. soc. chim. Belg.*, 1927, 36, 206; *Brit. Chem. Abs.* A, 1927, 452.
[17] *Ber.*, 1903, 36, 1499.
[18] Stephens, *J.A.C.S.*, 1928, 50, 568.
[19] *Ber.*, 1930, 63B, 2362; *J. Russ. Phys.-Chem. Soc.*, 1930, 62, 2051; *Chem. Abs.*, 1931, 25, 2044.
[20] *Ber.*, 1913, 46, 2952; *Chem. Abs.*, 1914, 8, 117.

Later, Medvedev and Alekseeva[21] oxidized cyclohexene in the presence of a less active catalyst, osmium dioxide deposited on asbestos. The activity of this catalyst was greatly reduced when metallic oxides such as aluminum oxide, ferric oxide, manganese sesquioxide, or cupric oxide were substituted for the asbestos. These investigators also observed that the oxidation products formed depend upon the nature of the solvent and that, contrary to Willstätter and Sonnenfeld, oxidation with this mild catalyst proceeds energetically in benzene. The products obtained from the oxidation of cyclohexene were 2-cyclohexene-1-ol, adipic acid, an unidentified aldehyde, and some peroxides.

The oxidation of cyclohexene may also be accomplished with lead tetrasalts[22] (lead tetra-acetate, tetrabenzoate, and others). For example, cyclohexene is oxidized with lead tetra-acetate at 80° C. to yield 2-cyclohexene-1-ol acetate. Cyclopentadiene, however, oxidized at 40° to 45° C., yields two products: 3-cyclohexene-1,2-diol diacetate and the monoacetate monoacetylglycolate of this diol. These results, together with those obtained with many other unsaturated compounds, indicate that the lead salts react in two ways: (1) by the addition of two acid groups to the double bond, and (2) by the replacement of hydrogen by a hydroxyl group while the double bond remains unattacked. In no instance did substitution alone take place.

Staudinger and Lautenschläger[22a] measured the velocity of autoxidation of trimethylethylene, styrene, isoprene, dimethylbutadiene, cyclopentadiene, tetrahydrobenzene, myrcene, limonene, terpinene, pinene, and menthene in sealed vessels at 80° C. and determined the oxygen absorbed. The rate of polymerization was approximated by heating 10 grams of the substance in a distillation flask in the presence of carbon dioxide or oxygen for various periods and removing all the matter volatile below 80° C. under reduced pressure. In all cases polymerization occurred more rapidly in oxygen than in carbon dioxide but the differences were small for the terpenes. From this it is concluded that autoxidation accelerates polymerization. The behavior of 1,5-hexadiene, 2,4-hexadiene, 2-methyl-2,4-pentadiene and 2,3-dimethyl-1,3-butadiene on autoxidation was studied by Kogerman.[22b] Practically no oxygen was absorbed during 3 months at 19° to 27° C. Two moles of oxygen per pair of double bonds were absorbed by 2,4-hexadiene and 2-methyl-2,4-pentadiene, but 2,3-dimethyl-1,3-butadiene absorbed only 1 atom of oxygen per molecule. The resulting compounds were similar to gums in cracked gasoline. Kogerman believed that a 1,4 addition of oxygen occurs in hydrocarbons with conjugated double bonds.[22c]

GUM IN GASOLINE

Among the early investigators who observed the autoxidation of light petroleum distillates was Fudakowski.[23] After shaking "commercial benzine" with a large volume of air in sunlight he found that the liquid became "activated," and that water extracted a neutral substance, apparently hydrogen peroxide. Longer exposure to air and light, followed by extraction with water, indicated that formic acid had been produced by the action of air on the distillate. The air above the distillate gave tests for what Fudakowski designated as "ozone." Similar results were obtained by Schaer[24] with American oils.

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[21] *Papers Karpov Chem. Inst. Bach Memorial Vol.*, 1927, 110; *Chem. Abs.*, 1928, **22**, 3086.

[22] Criegee, *Ann.*, 1930, **481**, 263; *Chem. Abs.*, 1930, **24**, 5286.

[22a] *Ann.*, 1931, **488**, 1; *Brit. Chem. Abs.* **A**, 1931, 1031.

[22b] *Trans. 2nd World Power Conf., Berlin*, 1930, **8**, 33; *Chem. Abs.*, 1931, **25**, 5549.

[22c] *Cf.* Martin, Gruse and Lowy, *Ind. Eng. Chem.*, 1933, **25**, 381.

[23] *Ber.*, 1873, **6**, 106; *Chem. Soc. Abs.*, 1873, **26**, 594.

[24] *Ber.*, 1873, **6**, 406; *Chem. Soc. Abs.*, 1873, **26**, 839.

Robinson [24a] noticed that water shaken up with light distillate of petroleum gave various aldehyde reactions, indicating the presence of acetaldehyde (estimated at 0.001 per cent). The formation of acetaldehyde was accounted for by the decomposition of some oxygen-containing compounds in the crude oil. However, Kramer [24b] searched for acetaldehyde and ketones in oils but did not detect their presence.

Schönbein [25] observed that a small proportion of resins was also formed under these conditions in addition to formic acid and its homologues. A part of the dissolved oxygen is in a very active state. He also noted the formation of "ozone" in the air above the distillates.

From our present knowledge of the autoxidation of unsaturated hydrocarbons it is very probable that the "ozone" thus reported was the vapor of the peroxides formed by oxidation. The formation of resins or gums by the oxidation of distillates on exposure to air, as well as its prevention, has become of paramount interest, particularly since the introduction of cracked gasoline as an antiknock fuel. Hunn, Fischer and Blackwood [26] discussed methods for the determination of gum in gasoline and the behavior of gasolines of different gum contents during engine tests.

Cracked gasoline as it comes from the stills usually contains very little, if any, gum but it does contain certain hydrocarbons (unsaturated compounds) which form gum on storage. Gum formation is essentially an oxidation process, and the gum itself contains a high percentage of oxygen. Gasolines stored in the absence of air show no increase in gum content.

The gum formed by oxidation during storage is of particular interest as it remains dissolved in the gasoline except in extreme instances when part of it precipitates. This gum is sprayed from the carburetor with the gasoline and is deposited on the heated portions of the intake manifold and on the intake valves, causing imperfect operation of the engine through the delayed seating of these valves. Only a portion of the dissolved gum, however, is deposited, the remainder being carried into the combustion chamber to be burned with the charge.

The determination of dissolved gum,[27] and of the stability of the gasoline is of importance. The product marketed must be sufficiently stable toward oxidation to keep the dissolved gum content below the permissible maximum until the time of consumption.

The usual copper-dish method for the determination of the gum content, which consists in evaporating 100 cc. of the gasoline in a copper dish on a steam bath, has been found to yield erratic and unreliable results. As pointed out by Voorhees and Eisinger,[28] the results obtained by this test vary, being dependent upon the rate of evaporation and accompanying oxidation and upon the catalytic action of the copper during evaporation. Voorhees and Eisinger agree with Hunn, Fischer and Blackwood that a gasoline which shows a high gum content by this test may perform satisfactorily in an engine.

Hunn, Fischer and Blackwood suggested that the dissolved gum content be determined by directing a jet of air towards the center of a 100 cc. sample of gasoline which is being evaporated in a glazed porcelain dish on a steam bath. As much air as possible should be used in order to cause complete evaporation in 12 to 15 minutes. The residue is then dried at 100° to 105° C. until constant weight is obtained.[29] Nitrogen or carbon dioxide may be substituted for air. The results with either of these gases agree with those obtained with air, indicating that no appreciable oxidation takes place during the short time required for evaporation. Mulligan, Lovell and Boyd [29a] modified this method of determination of gum content by substituting a heated jet of air for the unheated air.

[24a] *J.S.C.I.*, 1899, **18**, 232; *Chem. Zentr.*, 1899, **1**, 1065. See Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, **1**, 431.

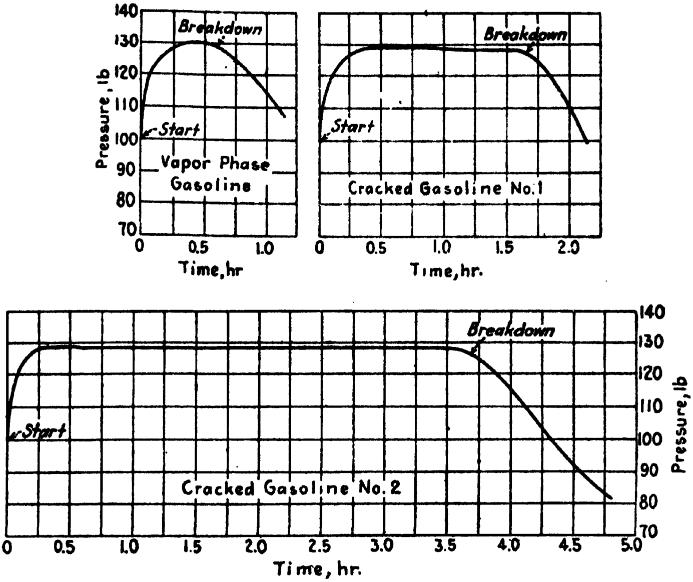
[24b] See Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, **1**, 431.

[25] *J. pr. Chem.*, 1866, (1) **98**, 257; *ibid.*, 1867, (1) **100**, 496; *ibid.*, 1867, (1) **201**, 145; see also Engler-Höfer, *op. cit.*, **1**, 517.

[26] *S.A.E. Journal* (*Penn. Sect. Paper*), 1930, **26**, 31; *Nat. Pet. News*, 1929, **21** (43), 65; *Chem. Abs.*, 1930, **24**, 2280.

[27] Voorhees and Eisinger, *Oil and Gas J.*, 1928, **27** (31), 155, 159; *Chem. Abs.*, 1929, **23**, 2286. *Cf.* Bespolov and Degtyareva, *Aserb. Neft. Khos.*, 1932, **6**, 118; *Brit. Chem. Abs.* **B**, 1933, 99.

[28] A summary of these tests is given by Kalichevsky and Stagner, "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933, 319. Bridgeman and Aldrich (*Oil and Gas J.*, 1931, **29** (37), 42; *Chem. Abs.*, 1931, **25**, 1980) compared gum determinations by the copper dish and air-jet methods. Some proposed A.S.T.M. methods have also been described (see *Proc. Am. Soc. Testing Materials*, 1932, **32**, Part 1, 412; *Chem. Abs.*, 1933, **27**, 1742).



Courtesy of S.A.E. Journal.

FIG. 32.—Typical Oxidation Stability Curves of Gasolines.

(These show the definite instability of the Vapor-Phase Gasoline, the slightly greater stability of Cracked Gasoline No. 1, and the marked stability of Cracked Gasoline No. 2, which can be stored for prolonged periods.) (Hunn, Fischer and Blackwood.)

The following method of determining the stability of a gasoline was suggested by Hunn, Fischer and Blackwood: A 100 cc. sample of the motor fuel in an 8-ounce bottle is placed in a bomb and oxygen is admitted until a gage pressure of 100 pounds per square inch is obtained (Fig. 33). The bomb is placed in a steam bath, and the pressure rises quickly to a maximum and remains constant, as shown by a recording gage, until oxidation starts. From then on the drop in pressure is very rapid (Fig. 32). A gasoline which will stand up for 1½ to 2 hours before "breakdown" occurs may be considered sufficiently stable for usual storage conditions.[30] Winning and Thomas [30a] suggested using the copper dish method in conjunction with the bomb test to predict the stability of gasolines.

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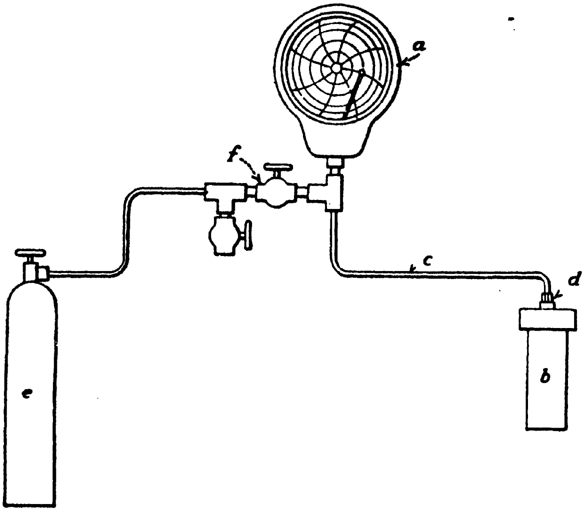
[29] The U. S. Bureau of Mines Steam Oven Test (Cooke, *U. S. Bur. Mines Rep.* 2686, 1925) gives essentially the same results.

[29a] *Ind. Eng. Chem.*, 1932, 4, 351; *cf.* methods of Norris and Thole (*J. Inst. Pet. Tech.*, 1929, 15, 681) and Mardles and Moss (*J. Inst. Pet. Tech.*, 1929, 15, 657).

Results obtained by actual engine tests [30b] indicate that a dissolved gum content of 15 mg. per 100 cc. is permissible. The usual copper-dish gum determinations give no indication of the quantity of gum deposit that might be formed in the engine. On the basis of engine tests, Voorhees and Eisinger [31] suggested 10 mg. of gum per 100 cc. of gasoline, as determined by the steam oven test, as a permissible quantity. They also indicated that the potential gum found in the oxygen test should not exceed 10 mg. per 25 cc. of gasoline.



Courtesy of S.A.E. Journal.

FIG. 33.—Apparatus for Measuring Stability of Cracked Gasoline toward Oxygen. (In making the accelerated oxidation test for gum formation, an open 8-oz. bottle containing the sample is placed in the Bomb *b*, the cover of which is screwed on tightly, and oxygen is admitted under pressure from the Cylinder *e*, until the pressure on the Recording Gage *a* registers 100 lbs., when the bomb is heated to 212° F. by a steam bath. The pressure then rises to a maximum that remains practically constant until oxidation starts and the gasoline breaks down. This point being indicated by a sharp break in the pressure curve drawn by the gage.) (Hunn, Fischer and Blackwood.)

Rogers, Bussies and Ward [31a] correlated results obtained by the Voorhees and Eisinger method with gum storage tests in glass bottles at 35° C.

The formation of gum during storage can be prevented, at least for long periods of time, by the addition of a small proportion of certain oxidation inhibitors to the gasoline.[32] The antioxidant efficiency of a number of these compounds (examined by the Voorhees method) shows that the induction period is directly proportional to the concentration of antioxidant.[33] The readily oxidizable monosubstituted p-aminophenols are particularly effective for this purpose. Egloff, Morrell, Lowry and Dryer[34] found that substances which contained phenolic or aromatic amine groupings had pronounced inhibiting power. Most of the effective compounds contained one of the following groupings: more than one hydroxyl or amine group, an aromatic hydroxyl and amine group, a single aromatic hydroxyl or amine group with one or more alkyl or other modifying groups, or an aromatic secondary amine grouping. Modifying groups in amines and phenols were most effective in the ortho or para position, but they exerted some beneficial influence when placed meta to the inhibiting group. The introduction of a nitro group into the phenols studied was generally disadvantageous. Hydrocarbons showed no positive inhibiting action nor did aromatic compounds which contained a halogen or other substituent group. Ethers exhibited no inhibiting properties but the presence of an amino group and an ether group in the same molecule had a slight beneficial influence. Ketones and quinones had variable effects as did acids and acid derivatives. Of the sulphur compounds, thiodiphenylamine showed marked inhibiting power.

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[30] The test suggested by Voorhees and Eisinger (*loc. cit.*) is to shake gasoline in long-necked Pyrex flasks filled with oxygen and placed in boiling water, and to note the decrease in pressure by a manometer. Oxidation appeared to be auto-catalytic as, in all cases, an induction period was noted. The duration of this induction period indicates the resistance of the gasoline to oxidation. The oxygen bomb test has also been described by Zublin, *Oil and Gas J.*, 1931, **30** (9), 26; *Chem. Abs.*, 1931, **25**, 5976.

[30a] *Ind. Eng. Chem.*, 1933, **25**, 511.

[30b] Marley and Gruse (*Ind. Eng. Chem.*, 1932, **24**, 1298) also studied gum deposition in engines.

[31] *Loc. cit.*

[31a] *Ind. Eng. Chem.*, 1933, **25**, 397.

Various substances have been suggested for the stabilization of gasoline by many investigators. Fischer and Gustafson[35] proposed α-naphthol, α-naphthylamine, and hydrocarbons such as naphthalene or anthracene with a hydroxyl or amino group in the α position. sec.-Amyl-p-aminophenol, hexyl-p-phenylenediamine, methylaniline, toluidine, aminophenol, resorcinol, tricresol, anthraquinone, and a dye (blue indophenol formed by the condensation of α- or β-naphthol with p-nitroso-dimethylaniline or the red indophenol obtained by condensing diphenylamine with p-nitrosophenol) have been suggested by Winning, Sargent and Dudley.[36] Oxazine, indamine, eurhodine, safranine, aposafranine and aminoazobases containing no sulphonic acid or thiobenzyl groups were recommended by Gutzeit.[37] Lewis and Mead[37a] proposed phloroglucinol, phenol, resorcinol, hydroquinone, thymol or pyrogallol. The Pure Oil Company[37b] suggested catechol, aniline, camphor, pyridine, tannic acid, nitrobenzene, amyl acetate and β-naphthol. Calcott and his co-workers proposed acyl derivatives of arylamines (acetanilide),[37c] methylaniline, ethylaniline, diphenylamine, 4-anilinobiphenyl, 2-methyldiphenylamine, ditolylamines and dixylylamines.[37d] Hyman and Ayers[37e] employed ammonia or its organic substitution products and catechol. The Gulf

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[32] Oxidation inhibitors can be used with many other substances, for example, fats, fatty acids, soaps and rubber. For a study of a large number of such inhibitors see Smith and Wood, *Ind. Eng. Chem.*, 1926, **18**, 691.

[33] Rogers and Voorhees, *Ind. Eng. Chem.*, 1933, **25**, 520.

[34] *Ind. Eng. Chem.*, 1932, **24**, 1375.

[35] U. S. Patent 1,904,433, April 18, 1933; *Chem. Abs.*, 1933, **27**, 3598; French Patents 681,707 and 681,708, 1929; *Chem. Abs.*, 1930, **24**, 4384; Canadian Patents 302,372 and 302,373, 1930; *Chem. Abs.*, 1930, **24**, 4386; German Patent 562,920, 1929; *Chem. Abs.*, 1933, **27**, 1162; all patents assigned to Standard Oil Development Co. *Cf.* Imperial Chemical Industries, Ltd., British Patent 366,041, 1929; *Chem. Abs.*, 1933, **27**, 1738.

[36] British Patent 383,511, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 4386.

[37] Canadian Patent 328,898, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 1501.

[37a] British Patent 318,521, 1929; *Brit. Chem. Abs.* **B**, 1931, 236; French Patent 681,064, 1929; *Chem. Abs.*, 1930, **24**, 4384; Canadian Patent 302,371, 1930; *Chem. Abs.*, 1930, **24**, 4385; German Patent 582,105, 1933; *Chem. Abs.*, 1933, **27**, 5182; all patents assigned to Standard Oil Development Co.

[37b] French Patent 701,340, 1930; *Chem. Abs.*, 1931, **25**, 4116.

[37c] Calcott and Lee, U. S. Patent 1,789,302, Jan. 20, 1931; assigned to E. I. duPont de Nemours and Co., Inc.; *Brit. Chem. Abs.* **B**, 1931, 873.

[37d] Calcott and Walker, British Patent 388,826, 1933; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1933, **27**, 4665.

[37e] British Patent 364,533, 1930; *Chem. Abs.*, 1933, **27**, 2027.

Refining Company[87f] suggested stabilizing gasoline with a substance which increases the period of induction of gum, such compounds being α-naphthol, pyrogallol, triphenyl phosphate, benzidine, ortho-, meta- and para-toluidine, together with a substance which reduces the rapidity of formation after the period of reduction, for example, α- and β-naphthylamines, diphenylamine, dimethylaniline, amyl alcohol, triphenylcarbinol and xylidine.

Rather, Beard and Reiff recommended an alkaloid[87g] such as brucine in a butyl alcohol solution and nicotine or thiocarbanilide.[87h] Jaeger employed various imidines[87i] and phthalide compounds and aniline.[87j] Phosphatides of animal or vegetable origin were recommended by the Hanseatische Mühlenwerke A.-G.[87k] A semicarbazide or a derivative of semicarbazide such as 4,4-diphenylsemicarbazide, or a hydrazine containing an aromatic radical, for example, unsym.-diphenylhydrazine, was suggested by Burk,[87l] and a small amount of crude petroleum spirit distilling above 140° C., by Vellinger and Radulesco.[37m] Selenomercaptans such as phenyl selenomercaptan also stabilize gasoline, according to Rosenstein and Hund.[87n] Ward, Jordan and Fulweiler[87o] found that mercaptans catalyze and phenols retard gum formation and that stannic chloride and antimony chloride remove gum-forming constituents. Lowry and Dryer,[87p] to stabilize gasoline, add a small quantity of the tar fraction obtained from the destructive distillation of wood.

Egloff, Morrell, Lowry and Dryer[87q] established a correlation between the effectiveness of gasoline inhibitors and their critical oxidation potentials. The results indicated that the best inhibitors had potentials between 0.6 and 0.8 volts but fair inhibitors occur in the range of 0.8 to 1.043 volts. Compounds having potentials above 1.043 volts were observed to have no inhibiting action under the conditions of the test.

Schuemann[87r] proposed a "gum-inhibiting index" defined as:

$$\text{Gum-inhibiting index} = \frac{(\text{Average percentage of potential gum reduction})}{(\text{Average concentration of inhibitor in mg. per 100 cc.})}$$

to show the efficiency of an inhibitor.

Ramsay[88] extended the study of the accelerated gum test by varying the time, oxygen pressure, and temperature of heating. Comparison of the weight of gum formed with the induction period indicated that the steam-oven test gives a reliable index of the stability of the gasoline in storage. Ramsay also observed that the induction period with 100 pounds per square inch oxygen pressure could be multiplied by 1.41 to give the induction period for air at 1 atmosphere pressure. When the induction periods were plotted against the absolute temperatures, on semi-logarithmic coordinate paper, a linear relation was established and the curve could be extrapolated to give the induction period at ordinary temperatures. The general equation for such curves is:

[87f] French Patent 742,716, 1933; *Chem. Abs.*, 1933, 27, 3598.

[87g] U. S. Patent 1,909,985, May 23, 1933; assigned to Socony-Vacuum Corp.; *Chem. Abs.*, 1933, 27, 4067.

[87h] U. S. Patents 1,916,437 and 1,916,438, July 4, 1933; *Chem. Abs.*, 1933, 27, 4662.

[87i] U. S. Patent 1,908,705, May 16, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, 27, 3805.

[87j] U. S. Patent 1,914,509, Jan. 20, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, 27, 4388.

[87k] French Patent 744,594, 1933; *Chem. Abs.*, 1933, 27, 4388.

[87l] U. S. Patent 1,906,044, April 25, 1933; assigned to Standard Oil Co. of Ohio; *Chem. Abs.*, 1933, 27, 3600.

[37m] *Compt. rend.*, 1933, 197, 417; *Brit. Chem. Abs.* B, 1933, 773.

[87n] U. S. Patent 1,835,184, Dec. 8, 1931.

[87o] *Ind. Eng. Chem.*, 1932, 24, 969, 1238.

[87p] U. S. Patents 1,889,835 and 1,889,836, Dec. 6, 1932; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, 27, 1744. Egloff, Morrell, Lowry and Dryer (*Oil and Gas J.*, 1933, 31 (45), 64; *Chem. Abs.*, 1933, 27, 3594) give results obtained by the use of this "Universal Inhibitor."

[87q] *Ind. Eng. Chem.*, 1933, 25, 804.

[87r] *Natl. Petroleum News*, 1933, 25 (14), 29; *Chem. Abs.*, 1933, 27, 3594.

[88] *Ind. Eng. Chem.*, 1932, 24, 539. See also Ramsay and Davis, *Ind. Eng. Chem.*, 1933, 25, 934; 'drich and Robie, *S.A.E. Journal*, 1932, 30, 198T; *Chem. Abs.*, 1932, 26, 3656.

$$\log I = a - bT$$

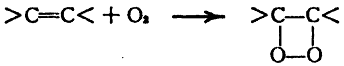
in which I is the induction period, T is the Centigrade temperature, and a and b are specific constants for each gasoline. The ratio of a to b, however, did not give the exact slope of the straight line, and the induction periods at two different temperatures, at least, should be determined in order to obtain, by extrapolation, the induction period at ordinary storage temperatures.

Although the actual mechanism of gum formation has not yet been determined, nevertheless all investigators agree that gum is an oxidation product and that peroxides are formed as intermediates.[38a]

Several methods have been devised for the estimation of the peroxides formed by the oxidation of unsaturated hydrocarbons but none of them appears to be entirely satisfactory. All are based upon the oxidizing property of the peroxides.

Stephens[39] attempted to determine the peroxide oxygen in cyclohexene peroxide with stannous chloride. The method, however, gave low results. The total oxygen by difference, after determining the carbon and hydrogen contents by combustion methods, nevertheless, checked with the theoretical values. Marks and Morrell,[40] who worked with linseed oil and similar products, suggested that the sample be dissolved in glacial acetic acid, and a concentrated solution of potassium iodide be added, after which the liberated iodine can be titrated with thiosulphate. A possible source of error in the general use of this method is that in some instances the iodine may react with a portion of the unsaturated hydrocarbons present. Yule and Wilson[41] allowed the peroxides to react with ferrous sulphate, in a water-acetone solution, and determined the ferric sulphate formed by titration with titanous chloride. From the quantity of ferric sulphate formed the "peroxide number" was calculated. This peroxide number is defined as the number of gram equivalents of active oxygen per 1000 liters of gasoline. The last method, though rapid and sufficiently accurate for studying gum formation in gasoline, is open to two objections. (1) It cannot be used when the peroxide number exceeds 10. If this is the case, the sample must be diluted with a peroxide-free gasoline before test. (2) A correction factor has to be applied. The corrections are calculated by making the arbitrary assumption that the method gives a correct result for samples with a peroxide number of 3. The observed values are always lower than the corrected ones. The corrections with peroxide numbers of about 3 to 5 are small but become quite appreciable with numbers of 8 to 10. Variations in the concentration of the reagents are said to alter the results.

Peroxides are, as stated previously, the first products of the oxidation of unsaturated compounds by air, oxygen of the air uniting with the molecule at the double bond:



$$>C{=}C< + O_2 \longrightarrow \begin{array}{c}>C-C<\\ |\quad\;|\\ O-O\end{array}$$

The rate of formation of these peroxides is greatly affected by the presence of small quantities of positive or negative catalysts, and by the temperature at which oxidation takes place. The temperature coefficient, however, is rather difficult to determine because of the lack of accurate data for the solubility of oxygen in gasoline at various temperatures.

[38a] Naphtali (*Chem.-Ztg.*, 1930, 54, 371; *Chem. Abs.*, 1930, 24, 3892) summarized the work of various investigators in this field and showed that it substantiates the theory that gum-formation is associated with oxidation.

[39] *Loc. cit.*

[40] *Analyst*, 1929, 54, 503; *Chem. Abs.*, 1929, 23, 5439.

[41] *Ind. Eng. Chem.*, 1931, 23, 1254. This article gives an excellent review of the properties and the methods of determination of peroxides.

The induction period observed in the oxidation of gasoline may be due to either of two causes: (1) the slow initial formation of peroxides which, after a certain concentration is reached, actually catalyze the oxidation and (2) the naturally occurring inhibitors which delay the reaction until they have been oxidized.

Peroxides react with reducing agents (hydrogen, hydrogen sulphide, or mercaptans) to form either glycols or substituted ethylene oxides. With lead mercaptides they yield substituted ethylene oxides, lead oxide, and disulphides. Sulphur dioxide reacts in a similar manner with the peroxides, being converted to sulphur trioxide. Solutions of sodium hydroxide convert peroxides into alcohols and sodium salts of acids. Concentrated sulphuric acid readily decomposes peroxides and assumes a deep red color.

Although the peroxides are stable at room temperature and can be kept for long periods, nevertheless decomposition or reaction with unsaturated hydrocarbons present occurs. These decomposition or reaction products are probably the source of gum for, in many instances, the quantity of gum obtained on evaporation of the sample, is proportional to the peroxide number.

The presence of peroxides is, no doubt, the explanation of the decomposition observed by Ellis and Wells[42] during the distillation of a cracked gasoline which had stood for some time and also for the explosion which occurred when the residue from distillation *in vacuo* was heated with a little sulphur.

Yule and Wilson[43] suggested that the gum in gasoline, particularly during storage, is present entirely in the peroxide form. Actual gum is not obtained until the gasoline is evaporated and the residue heated. All peroxides do not form gum since some of them are volatile. The actual mechanism of gum formation has not yet been definitely established.

Cassar[44] showed that simple olefins, when added to olefin-free gasolines (to the extent of 20 per cent or less), do not produce gum on evaporation. When such mixtures are subjected to an accelerated gum test for 4 hours little gum is obtained (under these conditions, most cracked gasolines yield large quantities of gum). When treated for 24 hours, however, gum was found. On the other hand, when diolefins such as dimethylbutadiene are added to olefin-free gasolines, large quantities of gum result on evaporation.

Brooks and Humphrey[44a] stated that tars sometimes observed in refining gasolines and kerosenes are due to the presence of diolefins. Cracked gasoline fractions which were found by Martin, Gruse and Lowy[44b] to give the greatest gum formation had boiling points corresponding to conjugated diolefins and cycloolefins. After the fractions were treated with maleic anhydride, or partially hydrogenated, or the gasoline was refined with sulphuric acid before fractionation, the fractions were more stable to oxidation at 38° but formed gum at 50° C., the maleic acid-treated one being the least, and the hydrogenated fraction the most, resistant. The stability at 38° C. was attributed to the removal of conjugated diolefins and the instability at 50° C. to the presence of cycloolefins.

Sulphuric acid converts olefins into gummy substances which are not volatile with steam and can be eliminated by distillation (see Chapter 26). The action

[42] *J. Ind. Eng. Chem.*, 1915, 7, 1029.
[43] *Loc. cit.*
[44] *Ind. Eng. Chem.*, 1931, 23, 1132.
[44a] *J.A.C.S.*, 1918, 40, 855.
[44b] *Ind. Eng. Chem.*, 1933, 25, 381.

of sulphur dioxide on olefins is negligible. This substance, however, promotes gum formation if the olefins contain peroxides, and such gum cannot be completely removed by washing with sodium hydroxide solutions. Washing with alkaline solutions reduces the gum content of stored gasolines which give a positive peroxide test with potassium iodide. The gum content of gasolines which do not give a positive test is increased in some instances and reduced in others. Peroxides were found to be strong knock-inducers and should therefore be removed before knock-rating is determined for the purpose of standardization. Removal of peroxides can be accomplished by washing with caustic alkali solutions [45] or by the addition of formaldehyde.

Flood, Hladky and Edgar [46] showed that aliphatic monolefins could be added to olefin-free gasoline in proportions up to 10 per cent by volume without producing gum on evaporation or a drop in pressure for 4 hours during the accelerated test. As the olefin content was increased, however, a shortening of the induction period was observed. Straight-chain olefins with double bonds near the end are more stable than those with double bonds in other positions. For olefins of similar structures those of low molecular weight are the least stable. Branched-chain compounds are less stable than straight-chain isomers. Naphthenic monolefins with a double bond in the ring are only slightly less stable than aliphatic monolefins. Naphthenes with a side-chain containing a double bond resemble the simple olefins. Aromatic compounds having a double bond adjacent to the benzene ring are particularly unstable. The diolefins as a class are unstable, but stability increases as the double bonds are more widely separated. For equivalent concentrations phenylbutadiene yields more gum than any other hydrocarbon investigated.

Analyses of various types of gum were made by Story, Provine and Bennett.[47] They found that gum can be divided into saponifiable and unsaponifiable portions, and that some of the acids obtained from the saponifiable portion are soluble and others insoluble in water. A typical analysis of gum obtained by the evaporation of a cracked gasoline in a copper dish is given in Table 142.

TABLE 142.—*Composition and Characteristics of Gum (from Copper Dish).*

	Original Gum 100 Per Cent	Unsaponifiable Matter 13.00 Per Cent	Insoluble Acids 55.00 Per Cent	Soluble Acids 30.50 Per Cent
Carbon	70.73	64.20	73.22	66.70
Hydrogen	6.95	6.32	6.81	7.20
Oxygen	19.51	13.81	18.58	24.23
Nitrogen	0.13	Trace	Nil	Nil
Sulphur	0.68	0.29	0.41	1.07
Ash	2.00	15.38	0.98	0.80
Hanus iodine value	73	—	89	84
Molecular weight	200	—	119	—
Saponification value	191	0	104	94
Neutralization equiv.	732	0	460	241
Melting point	98°-105° C.	—	192°-195° C.	—
Physical nature	Dark brown resinous	Dark brown solid	Light brown solid	Brown viscous liquid

[45] *Cf.* Yule and Wilson, *loc. cit.*
[46] *Ind. Eng. Chem.*, 1933, 25, 1234; see Kalichevsky and Stagner, *op cit.*, 316.
[47] *Ind. Eng. Chem.*, 1929, 21, 1079.

The ash was considered to be largely dust particles accumulated during evaporation of the oil in dishes.

Gum formed in sunlight from a vapor-phase cracked gasoline yields similar products and volatile acids in addition. The gasoline itself contained some volatile and non-volatile acids which could be extracted together with phenols by sodium hydroxide solutions. Acetic and acrylic acids were identified among the low-boiling acids. Acidity and peroxide and gum formation increase with the time of exposure to sunlight, but no direct relation between them could be established. Different rates of acid formation were observed during evaporation of the gasoline in copper and in glass dishes, the former giving the higher rate. Gum itself gives no test for peroxides, and only faint tests for aldehydes and ketones. It was suggested that the mechanism of gum formation is: Olefin → Activated Olefin → Peroxide → Polymerized Acids and Higher Aldehydes and Ketones.[47a]

Freund[47b] found that the gum content of cracked gasolines increases with the length of exposure to ultraviolet radiation. Smaller amounts of gum were formed in straight-run benzines, paraffin, naphthene, and aromatic and simple unsaturated hydrocarbons under the same conditions. This led to the belief that complicated unsaturated hydrocarbons are the gum-forming constituents and that absorption of oxygen plays only a secondary rôle in this type of gum formation. On the other hand, Vellinger and Radulesco[47c] observed that the amount of gum formed on exposure to radiation from a mercury lamp is a function of the speed of absorption of oxygen. Gasolines were exposed in atmospheres of oxygen in closed containers. At the start the quantity of gum formed was nearly proportional to the amount of oxygen absorbed but as exposure continued, absorption of oxygen diminished and gradually approached a limit which depended upon the pretreatment of the sample.

Although the subject of refining is beyond the scope of this book,[48] some of the methods of removing gum are directly pertinent to this subject and deserve brief mention by way of illustrating the methods in general. In Chapter 26 some treatments for the removal of gum-forming constituents by polymerizing them in the presence of various contact materials have already been discussed. Stevens and Gruse[48a] heated gasoline distillates between 700° and 800° C. under a pressure of 1000 pounds per square inch. The undesirable substances polymerize and remain on distillation. Borax may be added to the distillate to cause polymerization.[48b] The distillate in this case is heated above room temperature but is kept below the cracking point. A mixture of ferric sulphate and fuller's earth may also be used in a similar manner.[48c] The addition of an aqueous solution of hydrogen chloride in the presence of aluminum, manganese, zinc, chromium, iron, cadmium, cobalt, nickel, tin, lead, antimony, boron, arsenic, copper or mercury has been suggested by Day,[48d] and Heath[48e] treats gasoline with an aqueous alkaline solution of potassium ferricyanide followed by a treatment with sulphuric acid.

[47a] *Cf.* Robinson, *loc. cit.*

[47b] *Brennstoff-Chem.*, 1933, 14, 61; *Chem. Abs.*, 1933, **27**, 3808.

[47c] *Compt. rend.*, 1933, **196**, 1495; *Chem. Abs.*, 1933, **27**, 4384.

[48] See Kalichevsky and Stagner, "The Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933.

[48a] British Patents 370,671, 370,672 and 372,928, 1932; *Chem. Abs.*, 1933, **27**, 3812; Canadian Patent 324,785, 1932; *Chem. Abs.*, 1932, **26**, 5412; all patents assigned to Gulf Refining Co.; *cf.* Holland, *Natl. Petroleum News*, 1931, **23** (52), 25; *Chem. Abs.*, 1932, **26**, 2309.

[48b] Morrell and Essex, U. S. Patents 1,890,229 and 1,890,230, Dec. 6, 1932; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 1744.

[48c] Cox and McDermott, British Patent 360,358, 1930; assigned to Refiners, Ltd.; *Brit. Chem. Abs.* **B**, 1932, 92.

[48d] Day, U. S. Patents 1,920,247 and 1,920,248, Aug. 1, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 4916.

[48e] *Petroleum*, 1931, **29**, 542; *Brit. Chem. Abs.* **B**, 1931, 829.

In other proposed methods the vapors of gasoline are brought into contact with materials which induce polymerization and separation of gum-forming constituents. Among the substances suggested are phosphorus pentoxide with the addition of metal halides or organic oxycompounds;[48f] copper;[48g] oxychlorides[48h] of tin, cadmium, copper and zinc; and a hot mixture of water, zinc and ammonium chlorides.[48i]

A preliminary induced oxidation and removal of gum-forming compounds has also been effected in both the liquid and vapor phases. In the liquid phase, oxidizing agents such as permanganates, lead dioxide, peroxides or persulphates[48j] are added to the gasoline. In the vapor phase, oxygen may be mixed with the gasoline vapors and the mixture injected into a closed chamber at a temperature of 150° to 175° C. The oxygen reacts with the undesirable compounds, the reaction products settling out.[48k] Baxter[48l] treats shale-oil gasoline with ozone, forming gum which is eliminated by centrifuging. This can be followed by a light acid treatment or an extraction with methanol. A mixture of sulphur dioxide and oxygen as the oxidizing gases in the presence of ferric sulphate is recommended by Egloff and Morrell.[48m]

Gum formation is prevented by Rather and Beard[48n] by passing an inert gas such as carbon dioxide or nitrogen countercurrent to a thin flow of gasoline. The inert gas removes any occluded air.

OXIDATION OF LUBRICATING OILS

All mineral lubricating oils absorb oxygen. The rate of absorption varies greatly with the nature of the oil, the extent of processing in refining, the temperature, and the presence of metallic catalysts. Most lubricating oils are used under conditions where a temperature rise occurs, and they are nearly always in contact with the oxygen of the air. Failures in lubrication, with accompanying damage to machinery, arise to a large degree from the oxidation of the lubricant, not because of any great loss of oiliness of the lubricant itself, but rather because oxidation yields viscous or solid bodies, or jelly-like emulsions with water, which interfere with the regular distribution of the lubricant at the bearing surfaces. One method of testing an oil for its behavior on oxidation consists of heating it to a given temperature and blowing oxygen or air through it for a specified time.[49] The quantity of asphaltic matter formed is then determined. In comparing eight oils of approximately the same viscosity at 93.3° C. (200° F.) obtained from widely different sources, Moore and Barrett[50] found them to differ greatly.

[48f] Malishev, *Petroleum Z.*, 1932, **28** (17), 7; *Chem. Abs.*, 1932, **26**, 4705.

[48g] Graves, U. S. Patent 1,867,697, July 19, 1932; assigned to Standard Oil Co. of Calif.; *Chem. Abs.*, 1932, **26**, 5200.

[48h] Sumpter, U. S. Patent 1,912,603, June 6, 1933; assigned to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 4386.

[48i] Kimball, U. S. Patent 1,917,648, July 11, 1933; *Chem. Abs.*, 1933, **27**, 4665. *Cf.* Lachman, *Natl. Petroleum News,* 1931, **23** (45), 32; *Oil and Gas J.*, 1931, **30** (26), 30; *Chem. Abs.*, 1932, **26**, 1425; see also Chapter 19.

[48j] Moreau, French Patent 748,267, 1933; *Chem. Abs.*, 1933, **27**, 5173.

[48k] Youker, U. S. Patent 1,910,734, May 23, 1933; assigned to Phillips Petroleum Co.; *Chem. Abs.*, 1933, **27**, 4069.

[48l] *Ind. Eng. Chem.*, 1929, **21**, 1096.

[48m] U. S. Patent 1,855,486, April 26, 1932; assigned to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1933, 295.

[48n] U. S. Patent 1,776,598, Sept. 23, 1929; assigned to Standard Oil Co. of N. Y.; *Chem. Abs.*, 1930, **24**, 5477.

[49] For a review of methods of testing sludging and gumming characteristics of oils see Kalichevsky and Stagner, *op. cit.*, 341.

[50] *J. Inst. Pet. Tech.*, 1926, **12**, 582; *Brit. Chem. Abs.* **B**, 1927, 132; *Chem. Abs.*, 1927, **21**, 1703.

Large increases in viscosity were found and these were greater with oils having high sulphur contents. Asphalt and acidity formation for each oil were roughly parallel. The methods used were the Michie sludging test (air blowing for 45 hours at 150° C.), and the British Air Ministry test (12 hours blowing at 200° C.).

In examining the fitness of oils for use in internal combustion engines, Hoblyn[51] employed evaporation tests at 250° C. in crucibles over an oil bath rather than blowing with air or oxygen. At regular intervals the loss was noted and the residue tested for soft asphalts, for asphaltenes soluble in carbon tetrachloride, and for "carbenes" insoluble in that reagent. The samples were also examined microscopically and engine tests of all the oils were made in typical automobile engines. When an oil which easily decomposed was subjected to the evaporation test, the soft asphalt content soon reached a constant value of about 3 per cent. The asphaltenes rose to 30 per cent after heating for 28 hours, after which carbenes were found. The carbenes then increased at the expense of the asphaltenes until at the end of 40 hours the content of soft asphalt was 3.28 per cent; of asphaltenes, 23.88 per cent; and of carbenes, 7.85 per cent. Photomicrographs showed early loss of homogeneity in the oil, increasing until the oil assumed a very dark mottled appearance.

Garner,[52] working with a series of lubricating oils from Texas and Pennsylvania crudes, found that oils of similar distillation range have similar evaporation losses at the same temperature, irrespective of their origin, and that carbonization (that is, the formation of asphaltenes) increases on heating much more rapidly than does the evaporation loss.

Chernojookov[53] has pointed out that the sludge from oxidation of refined oils may be formed in three ways:

(1) The unsaturated hydrocarbons, tars, and sulphur-containing substances on oxidation form a sludge consisting of asphaltenes and carbenes.

(2) The saturated hydrocarbons on oxidation form acids of high molecular weight which cannot be dissolved in petroleum ether and which have acid numbers varying between 60 and 110.

(3) Another sludge is obtained by the reaction of the metals with acids in the presence of water.

According to Chernojookov, the Conradson carbon appears to correspond only to the coke or carbon formed from asphaltenes and tars by evaporation of the oil. Saturated hydrocarbons (paraffins and naphthenes) do not form coke. Such carbonization values are, therefore, not representative of the oil in service. More reliable information appears to be obtainable by oxidizing the oil at high temperatures and pressures (150° C. and 15 atmospheres pressure) with air or oxygen. Treatment for 3 hours under these conditions seems to be sufficient.

An oxidation test giving some insight into the probable behavior of lubricating oils in engines was devised by Ehlers.[54] It consists of passing oxygen for 5 hours at the rate of two bubbles per second into 100 cc. of the oil heated to 170° C. Good oils yield no coke and only small quantities of tar.

In studying the deterioration of mineral oils Mead[55] and his collaborators used two methods. In one, the oil and oxygen are introduced into a closed system so designed that the quantity of oxygen absorbed by the oil can be determined by direct measurement. Between 120° and 130° C. the rate of disappearance of the oxygen is proportional to the time of exposure. The rate at 130° C., however, is 2.4 times as great as that at the lower temperature. At 120° C. and over small ranges (0.2 to 0.4 sq. cm. per gram) the surface exposed to the oxygen does not affect the rate of absorption. At higher temperatures, however, it may exert some influence. Sludge formation and acidity develop slowly at first, and the rate of sludge formation increases as oxidation is continued. The acidity developed probably catalyzes sludge formation. The rate of oxidation also appears to depend upon the degree of unsaturation.

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[51] *J. Inst. Pet. Tech.*, 1925, 11, 1; *J.S.C.I.*, 1925, 44, 274B.

[52] *J. Inst. Pet. Tech.*, 1921, 7, 98; *J.S.C.I.*, 1921, 40, 27R.

[53] *Ind. Eng. Chem.*, 1929, 21, 315.

[54] *Petroleum Z.*, 26, No. 15, *Motorenbetrieb und Maschinen-Schmierung*, 1930, No. 4, 3; *Chem. Abs.*, 1930, 24, 3350.

[55] Mead, Phelps, Washburn, Warner, Dirks, Bader and McCabe, *Ind. Eng. Chem.*, 1927, 19, 1240.

In the other method proposed by these investigators, the oil is heated to 150° C. Acidity development is autocatalytic only when the initial acidity is low. Sludge formation is greatly influenced by the initial acidity of the oil, larger quantities of sludge being formed when the initial acidity is high.

Haslam and Frolich[56] investigated the mechanism of oxidation of a highly refined oil. This oil was selected to eliminate, as far as possible, the effect of impurities. The oil (75 grams) was oxidized by passing through it dry oxygen at the rate of 10 liters per hour at 130° and at 140° C. The degree of oxidation, as indicated by the acidity, increases rather rapidly up to 28 hours, and from then on the increase is very slight up to 40 hours. The viscosity of the oil increases as oxidation progresses. The viscosity increases much more rapidly, however, after oxidation has apparently reached a maximum. Preheating the oil in the presence of nitrogen and the addition of the oxides of iron or copper or of various salts of copper catalyze the oxidation of the oil. Only a small proportion of the oxygen in the oxidized oils was found to be present as acids, the remainder being probably in the products of polymerization or condensation. On the basis of Bone's hydroxylation theory and the data obtained; the oxidation steps appear to be: Hydrocarbons → Alcohols → Aldehydes and Ketones → Naphthenic or Fatty Acids, or Condensation and Polymerization Products (Asphaltic Bodies).

That only a small portion of the dissolved oxygen remained in the oil, while the greater portion was present in the insoluble substances precipitated by the addition of petroleum ether, was pointed out by Waters.[57] The following results were obtained before and after exposing an oil for 23 days to the action of light and air:

	Carbon	Hydrogen	Oxygen
		Per Cent	
Original oil	86.37	13.73	—
"Insoluble product"	72.72	7.83	19.45
Filtered oil	84.49	13.42	2.09

The "insoluble product" was assumed to be of an acid character, for it readily dissolved in alcoholic potassium hydroxide.

The effect of metals and metallic oxides on the oxidation of petroleum was also investigated by Waters.[58] Two medium motor oils were used, one from a paraffin-base and the other from a naphthene-base crude. The oils were heated in an open container for 2 hours at 250° C. and the quantities of substances formed insoluble in petroleum ether were determined. It was observed that zinc and aluminum are without effect; steel, cast iron, nickel and cobalt cause a small increase; and phosphor bronze, brass and copper are distinctly active and effect an appreciable increase in the oxidation. Cupric oxide, nickelous and cobaltous oxides, and ferric oxide are also active. The greatest increases, however, are obtained by exposing the oils to air and light for 20 hours before testing. Later, Waters [59] observed that lubricating oils containing relatively high percentages of sulphur compounds are more easily oxidized either by heating or by exposure to air and sunlight than those of low sulphur content.[60]

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[56] *Ind. Eng. Chem.*, 1927, **19**, 292.
[57] *J. Ind. Eng. Chem.*, 1910, **2**, 452.
[58] *J. Ind. Eng. Chem.*, 1921, **13**, 901.

The oxidation of saturated paraffin oils which contain no sulphur compounds was investigated by Arditti [61] by bubbling air through them at different temperatures. The degree of oxidation of the oils was followed by measuring the change in the interfacial tension between 0.02 *N* sodium hydroxide solution and the oil, and by titration of the acidity with 0.1 *N* alcoholic potassium hydroxide solution. The first method indicated that no oxidation occurs at 15° or 85° C., but after 16 hours at 110°, 3 hours at 123°, and ½ hour at 150° C., marked changes had taken place in the oil. Great differences between the free and combined acidity of the oil were observed, which pointed to the occurrence of reactions of marked complexity.

The presence of metals often increases the resin content of lubricating oils. The extent of this deterioration appears to depend on the nature of the metals.[61a] It has also been suggested that the easily oxidizable constituents in the oils actually give off oxygen and thus contribute to the oxidation effect of metals. Borodulin [62] found that the oxidation of steel plates in contact with oils of varying resin content bears no relation to the latter, but depends principally on the viscosity of the oil. The protective action of oils on steel plates is enhanced by increasing their viscosity by the addition of resins. Oils from which resins have not been completely removed afford better protection than highly refined oils.

In a study of the effect of ozone on oils, Dover and Cromwell [63] used four unblended neutral mineral oils, two from paraffin and two from asphalt-base crudes. These oils were given a prolonged treatment with ozone after which the changes in their physical and chemical properties were determined. In all cases there was a decrease in the iodine number, an increase in the acid number, and but very slight change in the specific gravity. The viscosity was, however, generally increased by the treatment. The coefficient of static friction of the paraffin-base oils was reduced, but a less regular and pronounced change was observed in the asphalt-base oils. No general relation between any of the properties of the oils and their value as lubricants could be determined. It appeared, however, that an unsaturated oil would be a better lubricant than a saturated one.

In spite of the recognized deleterious effects of oxidation on mineral oils the proposal has been made to prepare certain lubricants by oxidation. For example, lubricating oil may be produced by blowing air or oxygen through a mixture of a hydrocarbon oil in which is dispersed a catalyst consisting of manganese, lead or mercury compounds. The temperature is maintained below the cracking point of the oil and blowing is continued until the acidity reaches about 1 per cent. The volatile products are allowed to escape. The oxidized oil can then be blended with other lubricating stock.[64]

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[59] *J. Ind. Eng. Chem.*, 1922, **14**, 725.

[60] The Waters and a number of other oxidation tests have been discussed by Nash and Bowen, "The Principles and Practice of Lubrication," Chapman and Hall, Ltd., London, 1929, 208.

[61] *Compt. rend.*, 1931, **192**, 944; *Chem. Abs.*, 1931, **25**, 4112; see also *Compt. rend.*, 1931, **193**, 589; *Brit. Chem. Abs.* **B**, 1932, 7.

[61a] Baader, *Elektrizitswirtschaft*, No. 461 and 463, 1928; *Chem. Abs.*, 1929, **23**, 2562; Boisselet and Mouratoff, *Chimie et industrie*, Special No., March, 1931, 410; *Chem. Abs.*, 1931, **25**, 3471.

[62] *Petroleum*, 1927, **23**, 1515; *Brit. Chem. Abs.* **B**, 1928, 148.

[63] *Ind. Eng. Chem.*, 1927, **19**, 94.

[64] Harger, British Patent 167,789, 1920; *Chem. Abs.*, 1922, **16**, 305; Stuart and Stuart, British Patent 367,848, 1930; *Chem. Abs.*, 1933, **27**, 2293.

OXIDATION INHIBITORS FOR LUBRICATING OILS

Haslam and Frolich[65] found that certain substances acted as negative catalysts, that is, delayed the oxidation of mineral oils for a period of time. After the catalyst had been eliminated either by oxidation, by decomposition by heating the oil or by evaporation, oxidation took place normally. The delay in hours when 0.01 gram of the negative catalyst was added to 75 cc. of the oil is given in Table 143.

TABLE 143.—*Oxidation Inhibition of Various Substances.*

Catalyst	Delay in Hours
β-Naphthylamine	3
Ethyl-α-naphthylamine	3
Methyl-α-naphthylamine	4.5
α-Naphthylamine	4.5
p-Aminophenol	5
Diphenylamine	5.5
Phenyl-α-naphthylamine	11
Diphenylhydrazine	18

The rate of oxidation of mineral oils and the formation of sludgy deposits can also be lessened by the addition of small quantities of cyclic amines or highly basic compounds[66] such as piperidine, diethylaniline or phenylenediamine.

Mead and his collaborators[67] tested a large number of organic negative catalysts or inhibitors and concluded that no generalization could be drawn as to the most effective type of compound. The substances which showed the greatest effect as inhibitors were sulphur,[68] nitrocresol and nitrobenzene. Small quantities of lead aryl or alkyl compounds (lead tetraethyl) have been suggested for preventing or hindering the partial decomposition and oxidation of mineral oils.[69]

Active inhibitors, according to Smith and Wood,[70] may be divided into two main groups: energetic reducing agents (stannous compounds and sodium thiosulphate) and strong bases (amines). The presence of such inhibitors increases general stability and resistance to oxidation. Their influence, however, is temporary, and their period of activity depends upon the concentration, the temperature, and the nature of the oxidation products formed. After the effect of the inhibitor or antioxidant is lost, the rate of oxidation is the same as that of the original oil. These substances, therefore, control oxidation for definite but limited periods of time. With basic inhibitors, combination probably takes place with the acid oxidation products, which are themselves good oxidation catalysts. The amines, because of the tervalent nitrogen with two partial valences, may form intermediate compounds with the easily oxidized ethylene hydrocarbons. In some instances, alcohols and phenols are effective as inhibitors. With certain of these (for example with eugenol), there is a concentration at which the substance is most active as an inhibitor, and above which it acts as a positive oxidation catalyst.

The inhibiting effects of a large number of nitrogen compounds were investigated by Moureu, Dufraisse and Badoche.[71] The secondary amines, diamines and aminophenols were found to be the most effective inhibitors. *N*-Methyl derivatives of diamines or aminophenols are said to be equally active. Substitution of both the amino and phenolic groups generally yields inactive compounds, but *N*-acyl derivatives, such as o-acetamidophenol, are still active inhibitors. Most amino-acids or amides have little or no inhibiting properties. Cyclic compounds containing a nitrogen atom in the ring (pyridine or quinoline) are only slightly active.

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[65] *Loc. cit.*

[66] Hofmann and Dunkel, British Patent 289,909, 1926; *Brit. Chem. Abs.* **B**, 1928, 514; *cf.* British Patent 262,107, 1925.

[67] *Loc. cit.*

[68] *Cf.* Waters, *loc. cit.*

[69] Callendar, King and Mardles, British Patent 295,230, 1927; *Brit. Chem. Abs.* **B**, 1929, 161.

[70] *Ind. Eng. Chem.*, 1926, **18**, 691.

OXIDATION OF TRANSFORMER OILS

The oxidation of transformer oils is very similar to that of lubricating oils, both as to mechanism and products formed. Since some of the work on the oxidation of transformer oils may shed light on the general mechanism of oxidation, it deserves attention here. The decomposition of transformer oil and the formation of sludge and other undesirable constituents can be prevented in actual use by maintaining a blanket of a non-reacting gas, such as nitrogen or carbon dioxide, over the oil.[72] However, as oxygen is soluble in the oil to some extent it is necessary to remove it either by vacuum treatment or by bubbling an inert gas such as nitrogen through the oil before it is charged into the transformer. Vacuum-treated oils undergo no changes when heated for several days in an atmosphere of carbon dioxide, even in the presence of metallic catalysts. Yamada[73] also showed that transformer oils which readily deposit sludge when heated in the presence of air yield no deposit and undergo no color change when heated in a vacuum or in the presence of nitrogen, carbon dioxide, or hydrogen, for 100 hours at 140° C.

Oxidation also depends to a large extent upon the degree of refinement of the oil. Highly refined oils are more easily oxidized than less refined oils. This is substantiated by oxidation tests made either by passing oxygen through the heated oil[74] or by heating a mixture of oil and oxygen under pressure.[75] Addition of unrefined oil or less refined oil to highly refined oil lessens the oxidizability of the latter. The protective action of the less refined or unrefined oils is probably caused by the presence of natural inhibitors which are eventually removed by the refining treatment.

The oxidation of transformer oils can be accelerated by the introduction of either metals or metallic compounds acting as catalysts. Lead and copper are particularly effective, and of these two, the lead is the more active. The rate of acid formation with lead as a catalyst is slow during the first hour of oxidation but thereafter increases rapidly. Various oils differ widely in their sludge-forming properties. Based upon the data he obtained, Butkow[76] suggested the following oxidation test for transformer oils: 100 cc. of the oil are heated to 120° C. in the presence of a piece of copper gauze (70 x 15 mm.) for 70 hours during which time a current of oxygen is admitted at the rate of 6 to 7 liters per hour. The oil is then poured into a graduated cylinder and the volume of sludge noted. The acidity and resin content of the oil are also determined.

Stäger and Bohnenblust[77] investigated the effects of suspending strips of metals and alloys in transformer oils heated to 112° C. for 1000 hours. Sludging is increased by the presence of copper, brass, tin, and zinc. Acid formation is greatly increased by copper and brass. Aluminum, iron and nickel have little effect. Lead, copper and zinc are attacked by the organic acids in the oil. Lead, in particular, tends to produce acids of low molecular weights which are insoluble in the oil. Resinous substances rich in oxygen, which appeared to be monocarboxylic acids, were also formed.

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[71] *Compt. rend.*, 1926, **183**, 408; *Brit. Chem. Abs.* **A**, 1926, 1031.

[72] Rodman and Maude, *Trans. Amer. Electrochem. Soc.*, 1925, **47**, 1; *J.S.C.I.*, 1925, **44**, 162B.

[73] *J. Soc. Chem. Ind., Japan*, 1930, **33**, 64B; *Brit. Chem. Abs.* **B**, 1930, 542.

[74] Tytschinin and Butkow, *Neft. Khoz.*, 1925, **8**, 38; *J.S.C.I.*, 1925, **44**, 746B. See also Yamada (*J. Soc. Chem. Ind., Japan*, 1931, **34**, supplementary binding 188; *Chem. Abs.*, 1931, **25**, 5009) who has shown that both acid and alcohol formation are smaller.

[75] Butkow, *Erdöl u. Teer*, 1927, **3**, 551; *Chem. Abs.*, 1927, **21**, 4058.

[76] *Neft. Khoz.*, 1924, **7**, 341; *J.S.C.I.*, 1925, **44**, 162B.

[77] *Bull. Schweiz. Elektrotechn. Ver.*, 1924, **15**, 93; *Chem. Zentr.*, 1924, **2**, 1420; *J.S.C.I.*, 1924, **43**, 898B; *Chem. Abs.*, 1925, **19**, 724.

In the oxidation of transformer oils at 120° C. by a stream of oxygen, von der Heyden and Typke[78] observed that the reaction is accelerated by the presence of sodium hydroxide, sodium or potassium carbonate, and ferric oxide. Magnesium oxide or carbonate give low values for both tar and acid. Lead monoxide decreases oxidation and lead dioxide greatly accelerates it, and red lead (Pb_3O_4) has little, if any, effect. Of the organic substances, phenol, starch, oxalic acid and oleic acid accelerate oxidation; and salicylic acid, hydroxylamine hydrochloride and especially pyrogallol and aniline have the opposite effect.

Anticatalysts or inhibitors of the same general type as those used with lubricating oils (that is, principally aromatic phenols and amines) can be used to reduce or prevent the oxidation of transformer oils. For example, Butkow[79] suggested adding 1 per cent of β-naphthol to the oil, and the British Thomson-Houston Co.[80] proposed to protect oils in actual use with quinol suspended in the oil at or near the surface exposed to oxidation. Amino-compounds such as urea, piperidine, diethylaniline or phenylenediamine, are said to protect the oil against both oxidation and polymerization.[81]

Other inhibitors which may be used are metallic soaps and adsorbents. By adding, for example, not more than 2 per cent of a neutral soap of aluminum, calcium, copper, lead, nickel, tin or zinc, the sludging tendency of the oil is reduced.[82] The soaps need not be soluble in the oil. The useful life of the oil may be prolonged two to three times by the addition of about 6 per cent of fuller's earth.[83] Mizushima and Yamada[84] also showed that free sulphur or organic sulphides such as isoamyl sulphide or selenium compounds are antioxidants for transformer oils.[85]

Some interesting information as to the mechanism of the oxidation of transformer oils has been given by Stadnikov and Vozzinskaia.[86] Data obtained by the systematic analysis of the deposit from used transformer oils indicated that sludge results from the condensation of resinous substances with organic compounds formed by oxidation of the oil. In these condensations the sulpho-acids or their sodium salts (present in oils that have been treated with sulphuric acid and imperfectly washed) act as catalysts. Only traces of such catalysts need be present, and they can exist in the oil in the form of emulsions invisible to the eye but visible under the microscope.

This view is further supported by the oxidation of acid-treated oils. One portion was treated with 90 per cent acid and another, with fuming acid (4.3 per cent SO_3). After careful washing, both were oxidized with air for 45 hours at 120° C. in the presence of copper gauze. Both oils showed increased acid and resinification numbers, but these increases were much less for the oil treated with 90 per cent acid. No solid deposits formed in either oil. These same oils were reoxidized after the addition of 0.1 per cent of naphthene sulphonic acids. They soon darkened and yielded considerable quantities of a brown precipitate. Oxidation was repeated in the presence of 0.2 per cent of the potassium salts of sulphonic acids and a much greater formation of the precipitate took place.

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[78] *Petroleum Z.*, 1927, **33**, 1253; *Brit. Chem. Abs.* **B**, 1927, 899; see also *Erdöl u. Teer*, 1927, **3**, 471; *Chem. Abs.*, 1927, **21**, 4058; *Typke, Z. angew. Chem.*, 1928, **41**, 418.

[79] *Erdöl u. Teer*, 1927, **3**, 267; *Chem. Abs.*, 1927, **21**, 2184.

[80] British Patent 212,928, 1924; *Brit. Chem. Abs.* **B**, 1926, 550.

[81] I. G. Farbenindustrie A.-G., French Patent 636,332, 1927; *Chem. Abs.*, 1929, **23**, 275.

[82] Evans, British Patent 267,174, 1925; assigned to C. C. Wakefield and Co.; *Chem. Abs.*, 1928, **22**, 1233.

[83] Cox, British Patent 278,365, 1927; assigned to British Thomson-Houston Co.; *Brit. Chem. Abs.* **B**, 1928, 843.

[84] *J. Soc. Chem. Ind., Japan*, 1929, **32**, 848; *Brit. Chem. Abs.* **B**, 1929, 931.

[85] *Cf.* Waters, *loc. cit.*

[86] *Trans. Karpov Inst. Chem.*, 1926, **5**, 109; *Chem. Abs.*, 1928, **22**, 2049.

A further indication of the condensing action of the naphthene sulphonic acids was obtained by these same workers[87] in the following manner: When the refined oil was heated in an atmosphere of carbon dioxide with acetic acid and cyclohexanol, the reaction was one of saponification only. If, however, naphthene sulphonic acids were present, resin-formation took place. Glacial acetic acid itself yielded resins with the naphthene sulphonic acids. As a test for naphthene sulphonic acids it is suggested that the oil be heated with acetaldehyde and acetic acid. A discoloration of the acetic acid layer indicates their presence.

In refining transformer oils, the oil, after washing with acid, is treated for about 1½ hours with silica gel. Silica gel replaces alkali for the elimination of excess acid, and the stability of the oil is improved because of the absence of alkali salts of organic acids. Air oxidation followed by a similar treatment with silica gel[88] has also been proposed as a substitute for the acid treatment.

Refining transformer oils by oxidation with air followed by precipitation of the oxidized substances by the addition of an alkaline reagent was suggested by Maloney.[89]

Evers,[90] however, believed that the sludge in transformer oils is the result primarily of a reaction of the oil with water and atmospheric oxygen, which is catalyzed by condensation in the capillary spaces of the insulated coils or other parts immersed in the oil. The oxidation products consist mainly of acidic compounds and partly of asphaltenes. These can be removed by treatment with fuller's earth at 60° C. Contrary to Butkow's results, Evers found that these products are not removed with silica gel.

EVALUATION OF TRANSFORMER OILS

The most important property of a transformer oil is its resistance to oxidation. A large number of tests have been devised for ascertaining the extent to which various oils possess this property. Some of the fundamental points which must be considered in making these tests are as follows:[91]

(1) Temperature. This varies between 100° C. and 175° C., but the temperature most generally used is about 110° C.

(2) Heating. A covered thermostat is better than an exposed oil surface on account of the variability of air currents.

(3) Container. Most metals act as oxidizing catalysts to some degree but glass apparently does not. A vessel of the same material should therefore be used in all tests to secure comparable results.

(4) Quantity of oil. This varies from 10 grams in the French method to 1000 cc. in the Swiss method. The ratio of volume of oil to exposed surface determines the speed of the reaction. A small surface is recommended as it prevents too rapid and uneven oxidation.

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[87] Stadnikov and Vozzinskaia, *Neft. Khoz.*, 1927, 12, 694; *Chem. Zentr.*, 1927, 2, 1915; *Chem. Abs.*, 1928, 22, 4240.

[88] Butkow, *Neft. Khoz.*, 1926, 10, 388; *Chem. Abs.*, 1927, 21, 2554.

[89] U. S. Patent 1,540,218, June 2, 1925; *Chem. Abs.*, 1925, 19, 2271.

[90] *Z. angew. Chem.*, 1925, 38, 659; *J.S.C.I.*, 1925, 44, 746B.

[91] Fachini and Borella, *Chem. Umschau Fette, Oele, Wachse u. Harze*, 1927, 34, 331; *Chem. Abs.*, 1928, 22, 4784.

(5) Catalyst. Copper in the form of a wire gauze or sheet is preferred. The total surface is of secondary importance.

(6) Air. The use of air or oxygen shortens the time but increases the manipulation required. It is unnecessary when copper is used.

(7) Electrostatic field. The obtainable information on this point is somewhat vague.

(8) Time. This varies from 5 hours to 24 days, and is arbitrarily selected. The Italian standard of 300 hours is long enough to yield sufficient quantities of oxidation products for the necessary determinations.

(9) Oxidation Products. The change in color of the oil is no criterion of quality. The total sediment (i.e., material insoluble in standard benzine) and the total acids (the intermediate products) should both be determined.

These oxidation products, in addition to being partially precipitated by the addition of petroleum ether, can also be extracted, because of their acid nature, by a solution of sodium hydroxide in 50 per cent alcohol (Kissling reagent). Kissling[92] suggested the terms "tar-forming value" and "coke-forming value" for mineral oils, effecting the separation of the two with the alcoholic sodium hydroxide reagent.

Numerous methods for making oxidation tests of transformer oils have been suggested. Stäger[93] proposed heating the oil at 112° C. for various periods up to 1000 hours. The sludge which separates is extracted with chloroform and weighed. The asphaltogenic acids in the weighed residue are determined by saponification with standard alcoholic alkali. The sludge insoluble in oil is determined by filtering the hot oil at 80° C. and weighing the residue. No direct relation was found between sludge formation and iodine number, formolite number, or other chemical characteristics.

Oxidation tests have also been devised by Butkow,[94] by Marcusson and Bauerschäfer,[95] and by Evers and Schmidt.[96] Butkow passed oxygen into an autoclave with some Wood's metal on the bottom heated at 150° C. in which glass tubes containing the oil are immersed. Subsequently the oil is treated with sulphuric acid, the acid layer is separated, and determinations are made of the acidity, sludge-formation, and saponification value.

The Marcusson and Bauerschäfer method is a modified sludge test in which sodium hydroxide is used as a catalyst. The oil is heated with pumice saturated with sodium hydroxide at 120° C. for 24 hours. To the mixture is then added alcoholic sodium hydroxide solution, with which it is refluxed for 20 minutes. The soap solution thus formed is separated, acidified, and the acids are extracted with benzene. The benzene extract is washed to remove any mineral acids, and the tarry material obtained by the evaporation of the benzene is weighed.

Evers and Schmidt compared the relative stabilities of various oils by heating them for 2 hours at 150° C. in the presence of silica gel impregnated with vanadium and ferric oxides and then determining their acid values. The test may be modified by heating the oil and oxygen in a closed container at 120° C. in the presence of the catalyst, followed by determination of the oxygen absorption. They expressed the opinion that oxidation is confined to unsaturated constituents.

In the test proposed by Matthis[97] the oil is heated under specified conditions and the time required for the formation of sludge is observed. The useful life of the oil in service is said to increase with the time required for the sludge to appear. By this method an experienced operator can detect the formation of 0.001 per cent of asphalt.

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[92] *Chem.-Ztg.*, 1907, **31**, 328; *J.S.C.I.*, 1907, **26**, 463. *Chem.-Ztg.*, 1908, **32**, 938; *J.S.C.I.*, 1908, **27**, 1053.

[93] *Helv. Chim. Acta*, 1923, **6**, 62; *Chem. Abs.*, 1923, **17**, 1851.

[94] *Neft. Khoz.*, 1927, **13**, 332; *Chem. Abs.*, 1928, **22**, 2458.

[95] *Petroleum Z.*, 1926, **22**, 572; *Chem. Abs.*, 1927, **21**, 1182; *Brit. Chem. Abs.* **B**, 1926, 427; *Chem. Ztg.*, 1926, **50**, 263; *Brit. Chem. Abs.* **B**, 1926, 427.

[96] *Wiss. Veröffentlich. Siemens-Konzern*, 1926, **5**, 210; *ibid.*, 1928, **7**, 343; *Brit. Chem. Abs.* **B**, 1927, 98; *Chem. Abs.*, 1929, **23**, 3565.

[97] *Rev. gén. électricité*, 1927, **21**, 901; *Chimie et industrie*, 1928, **19**, 62; *Chem. Abs.*, 1928, **22**, 1467.

Vanghelovitch[98] extended the method proposed by Hoblyn[99] by determining microscopically the time required for the precipitation of asphalt when the oil is heated at 250° C. The order of oxidation appears to be: Oil → Hard Asphalt → Soft Asphalt → Carbenes (colloidal carbon) → Coke. The heating may be avoided by another method in which the limiting concentration of nitric acid which will precipitate asphalt from the oil is determined. A thin film of the oil is placed under the microscope and a drop of nitric acid is added. This is repeated with solutions of various concentrations until precipitation of the asphalt occurs. The limiting concentration of nitric acid determines the resistance of the oil to oxidation. The results with nitric acid closely agree with those obtained by prolonged heating at 250° C.

According to Ford,[100] unsaturated hydrocarbons and naphthenes are both important in the oxidation of these oils. When over 5 per cent of unsaturated compounds is present, the quantity of sludge formed is independent of the source of the oil, i.e., whether the oil is of paraffin or asphalt base. Naphthene hydrocarbons of high molecular weight are less sensitive to oxidation than those of low molecular weight. Mixtures of the former with paraffins give oils highly resistant to oxidation and to sludging. No general rule can be given concerning the effect of different temperatures on the rate of oxidation of different oils. High temperature tests, however, did not agree with results obtained in actual use. Ford[101] devised a method for the determination of the different types of hydrocarbons in transformer oils.

TURBINE OILS

The oxidation of turbine oils is very similar in many respects to that of lubricating and transformer oils, so that it is unnecessary to discuss it in detail. In general these oils are affected by the same reagents, and oxidation tests can be carried out in practically the same manner as for the other two.

As an oxidizing test, Schmidt[102] recommended bubbling a slow stream of oxygen (2 bubbles per second) through 125 grams of oil heated to 100° C. Superficially oxidized copper gauze is also introduced into the oil and oxidation is continued for 70 hours. At the end of this time the acid number and the quantity of sludge are determined.

Rogers and Miller[103] suggested iron as a catalyst in a similar procedure. Butkow,[104] on the other hand, preferred to heat the oil with oxygen under 15 atmospheres pressure for 4 hours at 150° C. He also found that the highly refined turbine oils oxidize more readily than less refined ones.

The presence of small proportions of lead tetraethyl as an oxidation inhibitor in turbine oils, according to Hatta,[105] materially reduces the darkening of color and sludge formation in paraffin oils. With naphthene oils, however, although the darkening is retarded, the acid and sludge formation are increased. Oxidation tests in both instances were made at 120° C. with moist oxygen passed in at the rate of 150 bubbles per minute.

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[98] *Bull. soc. chim. Romania*, 1926, **7**, 93; *Brit. Chem. Abs.* **B**, 1926, 307.

[99] *Loc. cit.*

[100] *Ind. Eng. Chem.*, 1927, **19**, 1165.

[101] *Ind. Eng. Chem.*, 1927, **19**, 1165.

[102] *Z. angew. Chem.*, 1928, **41**, 1197; *Brit. Chem. Abs.* **B**, 1928, 918.

[103] *Ind. Eng. Chem.*, 1927, **19**, 308.

[104] *Erdöl u. Teer*, 1927, **3**, 823; *Chem. Abs.*, 1928, **22**, 863.

[105] *J. Soc. Chem. Ind., Japan*, 1925, **28**, 1346; *Chem. Abs.*, 1926, **20**, 816.

To prevent the formation of acids and the increase of emulsibility in use, Rogers[106] suggested adding an inhibitor containing either a hydroxyl or an amino group, such as diphenylamine, gallic acid, or dibutylresorcinol, to refined oils.

[106] U. S. Patent 1,774,845, Sept. 2, 1930; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1930, 24, 5149.

Chapter 41

Oxidation of Aromatic Hydrocarbons

The conversion of petroleum distillates into other products by vapor phase catalytic oxidation is a reaction of abundant promise and one which has received much attention. Since both aromatic and cyclic compounds have been isolated from petroleum fractions, the vapor phase oxidation of such hydrocarbons is of interest. As pointed out in Chapter 36, the oxidation of the vapors of some petroleum distillates has yielded maleic acid, and Ellis[1] obtained phthalic acid by oxidizing the vapors produced by cracking petroleum distillates.

Many petroleum fractions contain aromatic hydrocarbons and the isolation of some of these has already been described in Chapter 1. Mizuta,[1a] in determining the physical and chemical composition of Japanese gasolines, noted that fractions cut at 97° C., 120° C., and 150° C., contained benzene, toluene and xylene, respectively. Gasolines from crude oils from the southern part of the Japanese Archipelago were rich in aromatics and contained only a small proportion of naphthenes. The reverse was true of gasolines from the northern part. Zelinski and Juriev[2] observed that analytical determinations indicated as high as 16 to 17 per cent of aromatics in Ural benzine. Bruun, Leslie and Schicktanz[3] by careful fractionation have obtained, from an Oklahoma crude, a fraction boiling at 107° to 108° C. containing about 32 per cent toluene. This distillate on nitration yielded dinitrotoluene quantitatively.

Marek[3a] discussed methods and apparatus for the oxidation of hydrocarbons. He states that aromatics require high temperature and a catalyst and that the reaction proceeds in stages, hence a good yield of intermediate oxidation products can ordinarily be obtained. An extensive study of the vapor-phase catalytic oxidation of hydrocarbons has also been made by Wilken-Jorden.[3b]

The catalysts most extensively used in the vapor phase oxidation of aromatic compounds are oxides of the metals of the fifth and sixth groups of the periodic system, especially vanadium, uranium, tungsten and molybdenum. The metallic catalyst generally employed in the oxidation of aromatic hydrocarbons to acids appears to be vanadium. For producing aldehydes, other oxides, such as those of uranium or molybdenum, are used as they seem to be less energetic catalytic agents and hence more appropriate. Often a mixture of the oxides of these latter metals is more effective than the oxide of either metal alone.[4]

Reaction can be secured by passing the vapors of the aromatic compounds with air or oxygen over the heated catalyst, or by mixing a spray of a colloidal suspension of the oxide in the hydrocarbon with air in a heated reaction chamber. By the latter method Caspari[5] produced maleic acid from benzene, and benzaldehyde or benzoic acid from toluene.

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[1] U. S. Patent 1,516,720, Nov. 25, 1924; *Chem. Abs.*, 1925, **19**, 397; U. S. Patents 1,697,262 to 1,697,267, Jan. 1, 1929; *Chem. Abs.*, 1929, **23**, 1259; assigned to Ellis-Foster Co.

[1a] *Proc. World Eng. Cong.*, 1929, **31**, 31; *Brit. Chem. Abs.* **B**, 1931, 828.

[2] *Bull. Acad. Sci. U.S.S.R.*, 1930, 851; *Brit. Chem. Abs.* **B**, 1931, 661.

[3] *Bur. Standards J. Research*, 1931, **6**, 363; *Brit. Chem. Abs.* **B**, 1931, 660.

[3a] *Ind. Eng. Chem.*, 1932, **24**, 1103.

[3b] *J. Chem. Met. Mining Soc. S. Africa*, 1932, **32**, 248, 283, 322; *Brit. Chem. Abs.* **B**, 1932, 927; *Chem. Abs.*, 1932, **26**, 4941, 5406, 5744.

[4] For a very complete classification of these catalysts, see Craver, U. S. Patents 1,636,854 and 1,636,855, July 26, 1927; both patents assigned to Barrett Co. For the use of vanadium pentoxide, see Selden, British Patent 170,022, 1921; assigned to Selden Co.

In addition to the oxides, various salts of these same metals can be used, for example, a ferric vanado-chromate[6] or a complex vanadium pentoxide silicate.[7] The latter catalyst is not poisoned by sulphur compounds which may be present in the aromatic substances. "Zeolite" catalysts, or the reaction products of silicates with metallic salts such as potassium vanadate, are employed in the partial oxidation of aromatic hydrocarbons, or in the purification of such hydrocarbons by preferential oxidation.[8] The addition of stabilizers (the neutral or acid salts of the alkali and alkaline earth metals) and also of "stabilizer promoters" (compounds of heavy metals with amphoteric metals, e.g., aluminum, zinc or lead) to these catalysts is also recommended. These zeolites, after being used in oxidation processes, can be revivified by heating to 300° to 500° C. with halogens, non-metallic halides, acids or acid anhydrides, together with air or oxygen. The mass is subsequently mixed with hydrogen peroxide, which is removed later by evaporation. Or the catalytic mass may be heated to 300° C. in a stream of ozonized air.[9]

In catalytic vapor phase processes excessive oxidation of the aromatic compounds can be lessened by the addition of some other substance which is more readily oxidized.[10] For example, in the preparation of benzaldehyde or benzoic acid, methyl alcohol or gasoline vapors can be mixed with the vapors of toluene. Or gasoline vapors may be used similarly in the conversion of acenaphthene to naphthalic anhydride or of cresol to salicylaldehyde and salicylic acid.

Weiss, Downs and Burns[11] investigated the mechanism of the catalytic oxidation of benzene to maleic acid, particularly the oxide equilibria in the vanadium oxide catalyst. At 400° C. the catalyst at the end of the runs consisted of vanadium pentoxide and tetroxide, the proportion of the former increasing rapidly as the ratio of oxygen to benzene in the reacting gases increased. Even when the initial catalyst was a mixture of vanadium trioxide and tetroxide its final composition appeared to depend only on the ratio of oxygen to benzene. Catalytic action, therefore, appears to depend upon an oscillation between vanadium pentoxide and tetroxide, the dissociation of the former compound furnishing the activated oxygen.

At temperatures higher than 400° C., for any given ratio of air to benzene, the proportion of vanadium pentoxide decreased rapidly while complete combustion also increased at the expense of the partial oxidation products. The reverse was true at lower temperatures. Complete combustion is, therefore, not dependent on the ratio of vanadium pentoxide to tetroxide, but on some other factor, perhaps the activation of the reacting substances themselves.

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[5] U. S. Patent 1,674,589, June 19, 1928; British Patent 263,201, 1925; *Chem. Abs.*, 1928, **22**, 90.

[6] Meigs, U. S. Patent 1,486,781, Mar. 11, 1924; assigned to Carleton Ellis; *Chem. Abs.*, 1924, **18**, 1504.

[7] Monsanto Chemical Works, British Patent 298,142, 1927; *Chem. Abs.*, 1929, **23**, 2792. For the use of pyrovanadates, see Monsanto Chemical Works, French Patent 635,717, 1927; *Chem. Abs.*, 1928, **22**, 4678. Compagnie nationale de matières colorantes et manuf. produits chim. du nord réunies établissements Kuhlmann, French Patent 646,263, 1927; *Chem. Abs.*, 1929, **23**, 2256. Charlot (*Compt. rend.*, 1933, **196**, 1224; *Chem. Abs.*, 1933, **27**, 3454) determined the comparative volumes of carbon dioxide produced by air oxidation of toluene, diphenylmethane, naphthalene, alcohol, heptane, benzyl alcohol, xylene and benzoic acid in the presence of magnesium oxide, nickel oxide, molybdenum oxide, and tungsten oxide at 300° to 450° C.

[8] See Jaeger, U. S. Patents 1,678,626 and 1,678,627, July 24, 1928; 1,682,787, Sept. 4, 1929; 1,694,122, Dec. 4, 1928; 1,692,126, Nov. 20, 1928; 1,709,853, Apr. 23, 1929; 1,722,297, July 30, 1929; all assigned to Selden Co. British Patents 281,307, 1927; 291,419, 1927; 295,270, 1927; 296,071, 1927; 299,419, 1927; 300,968, 1927; 315,854, 1928; all assigned to Selden Co. Also, Selden Co., French Patent 649,292, 1927; *Chem. Abs.*, 1929, **23**, 2985. *Cf.* Jaeger, U. S. Patents 1,851,361, 1,851,362, 1,851,363, Mar. 29, 1932; assigned to Selden Co.; *Chem. Abs.*, 1932, **26**, 2987.

[9] Selden Co., British Patent 280,712, 1926; *Brit. Chem. Abs.* **B**, 1928, 90.

[10] Jaeger, U. S. Patent 1,909,354, May 16, 1933; *Chem. Abs.*, 1933, **27**, 3725; British Patent 348,604, 1930; both patents assigned to Selden Co.

[11] *Ind. Eng. Chem.*, 1923, **15**, 965.

The nature of the products of combustion must also be a function of some property of the catalyst other than the activation of oxygen by dissociation of the oxide. For example, there may be some specific relation between the structure and the dimensions of the metallic atom and the structures and the dimensions of the organic substances being oxidized. This surmise is illustrated in the case of benzene. The best catalyst for bringing about partial oxidation is an oxide of vanadium, though more complex molecules, such as naphthalene and anthracene, are susceptible to a large variety of catalysts. With benzene a mixture of various oxides will often effect partial oxidation, although the individual oxides do not possess this property.

Forrest and Frolich,[11a] however, maintain that with careful control of temperature and concentration of oxygen, aromatic compounds may be converted to partial oxidation products without the aid of catalysts. In their process, the heat of the oxidation reaction is compensated for by the latent heat of evaporation of the reacting material. By regulation of the pressure, thus causing evaporation or condensation, the temperature may be held practically constant. The pressures employed varied from 750 to 2500 pounds per square inch and the temperatures from 200° to 320° C. Toluene, for example, with 4.1 mole per cent oxygen under a pressure of 1000 pounds per square inch at 305° C. was converted after 30 minutes to benzoic acid, benzaldehyde, and carbon dioxide, corresponding to 24.8, 9.9, and 5.4 per cent, respectively, of the oxygen conversion. Other substituted benzene or polynuclear cyclic compounds such as cyclohexane[11b] may be used; with benzene itself, however, the ring is broken.

PRODUCTION OF MALEIC ACID

Kempf[12] was probably the first to obtain maleic acid by the oxidation of an aromatic compound. He oxidized quinone with silver peroxide (made by mixing solutions of silver nitrate and potassium persulphate) and the products were maleic and formic acids, carbon monoxide and dioxide.

Another procedure consists in passing equal weights of benzene vapor and air over a vanadium oxide catalyst at 400° to 450° C. at such a velocity that the time of contact is about 0.25 second.[13] Quinone may be added to the benzene, and the mixture similarly vaporized and catalytically oxidized to maleic acid. Inert gases may be used as diluents to control the reaction.[14] In addition to benzene, other aromatic hydrocarbons, e.g., toluene, can be oxidized to maleic acid in the presence of a vanadium oxide catalyst.[15] The temperature during oxidation may be regulated by passing the reacting materials over the catalyst supported on tubes which contain mercury. Vaporization of the mercury regulates the temperature and thus prevents overheating. The boiling point of the mercury can be adjusted by the application of pressure.[16]

[11a] U. S. Patent 1,902,550, Mar. 21, 1933; assigned to National Synthetic Corp.; *Chem. Abs.*, 1933, **27**, 3221.

[11b] U. S. Patent 1,916,923, July 4, 1933; assigned to National Synthetic Corp.; *Chem. Abs.*, 1933, **27**, 4540.

[12] *Ber.*, 1905, **38**, 3963; 1906, **39**, 3715.

[13] Weiss and Downs, U. S. Patent 1,318,633, Oct. 14, 1919; Canadian Patent 192,766, 1919; for the use of other metallic catalysts see U. S. Patent 1,318,631, Oct. 14, 1919; all patents assigned to Barrett Co. For the preparation of a catalyst carrier see Downs, U. S. Patent 1,636,685, July 26, 1927; U. S. Patent 1,672,308, June 5, 1928; both patents assigned to Barrett Co.

[14] Weiss and Downs, U. S. Patent 1,318,632, Oct. 14, 1919; assigned to Barrett Co.; *J.S.C.I.*, 1920, **39**, 44A.

Yabuta and Simose (*Bull. Inst. Phys.-Chem. Research, Tokio*, 1929, **8**, 197; *Chem. Abs.*, 1929, **23**, 3441) made a study of the influence of inert gases, the methods of preparing the catalyst, and the effect of acidic metal oxides in the catalyst on this oxidation.

[15] Weiss and Downs, Canadian Patent 235,972, 1923; assigned to Barrett Co.

Better yields of maleic acid or anhydride can be secured by using a mixed catalyst, for example, one which consists of vanadium pentoxide together with the higher oxides of molybdenum or uranium, or any of the oxides of the metals included in the fifth and sixth groups of the periodic system.[17] Not more than two such oxides should be incorporated in the catalyst. The temperature used with the various catalysts varies from 450° to 550° C. and the time of contact for the gases is about 0.3 second. These catalysts may be deposited on an inert porous carrier containing fused aluminum oxide.[18]

Alternate catalytic oxidation and decarboxylation may be applied to the stepwise degradation of aromatic hydrocarbons in the preparation of maleic acid.[19] For example, naphthalene and air can be passed over vanadium pentoxide at 400° C., then over cadmium oxide at 400° C., and finally over a mixture of cadmium and aluminum oxides at 380° C. At the end of these steps benzene is the principal product. Air is added to the benzene vapors and the mixture led over a vanadium pentoxide catalyst at 410° C. to form maleic acid, together with some benzoquinone.

Maleic acid can be obtained not only from aromatic hydrocarbons but also from other substances containing a ring structure, such as furane. In Chapter 36 it is pointed out that maleic acid is a product of the oxidation of gasoline vapors.[20] This may probably be due to the naphthenes present in gasoline. Ellis [21] showed that this same acid is formed, along with other dibasic acids, by the oxidation of the vapors from cracking kerosene and other petroleum fractions.

In another method, crude furfural was atomized with pure oxygen and passed over zinc vanadate or granulated aluminum at 300° to 350° C. The yield of maleic acid corresponded to about 30 per cent of the theoretical. Yields of about 50 to 60 per cent were secured when pyromucic acid was oxidized.[22] This process was somewhat modified by using furane with a large excess of oxygen or air (20 to 100 times the theoretical quantity) together with steam, the latter assisting in the vaporization of the furane.[23] The gaseous mixture was also passed over the catalyst at a lower temperature (about 180° C.).

By vaporizing furfuraldehyde in a current of air at 40° to 50° C. and leading the vapors over a vanadium oxide-asbestos catalyst at 200° to 300° C., a 14 per cent yield of maleic acid was obtained.[24] Other products formed at the same time are maleic anhydride, formaldehyde, water, and carbon dioxide, but no fumaric acid.

The oxidation of pyrroline derivatives by nitric acid to maleic acid derivatives was described by Ciamician and Silber.[25] Brominated thiophens on oxidation give the corresponding bromomaleic acids.[26]

[16] Weiss and Downs, U. S. Patent 1,374,720, Apr. 12, 1921; assigned to Barrett Co. See also Downs and Stupp, U. S. Patent 1,515,299, Nov. 11, 1924; assigned to Barrett Co.

[17] Craver, U. S. Patent 1,636,857, July 26, 1927; assigned to Barrett Co.

[18] Punnett, U. S. Patent 1,985,522, Jan. 31, 1933; assigned to National Aniline and Chemical Co.; *Chem. Abs.*, 1933, **27**, 2458.

[19] I. G. Farbenindustrie A.-G., British Patent 268,775, 1927; *Brit. Chem. Abs.* **B**, 1928, 598; Swiss Patent 127,034, 1927; *Chem. Abs.*, 1929, **23**, 1141.

[20] Shimose, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), 1931, 15, 251; *Brit. Chem. Abs.* **A**, 1931, 932.

[21] U. S. Patent 1,697,265, Jan. 1, 1929 (see Chapter 42).

[22] Zumstein, German Patent 478,726, 1927; assigned to C. H. Boehringer Söhne; *Chem. Abs.*, 1929, **23**, 4712. Also British Patent 285,426, 1927; *Chem. Abs.*, 1928, **22**, 4539.

[23] Boehringer, British Patent 297,667, 1927; *Chem. Abs.*, 1929, **23**, 2724.

[24] Sessions, *J.A.C.S.*, 1928, **50**, 1696. Milas (*J.A.C.S.*, 1927, **49**, 2005) reported a large yield of fumaric acid by the oxidation of furfuraldehyde with a solution of sodium chlorate in the presence of vanadium pentoxide.

[25] *Ber.*, 1887, 20, 698, 2594.

[26] Angeli and Ciamician, *Ber.*, 1891, **24**, 77, 1347.

The purification of crude maleic acid, made by the oxidation of benzene or naphthalene, by recrystallization from solvents (e.g., diethyl maleate or mixtures of the esters of maleic acid and hydrogenated polynuclear aromatic hydrocarbons) is described by Jaeger.[27] Iron compounds are removed from the crude acid by sodium cyanide.[28]

Maleic acid is converted to fumaric acid (the isomeric compound) by heating it either alone or in the presence of solvents, such as water[29] or benzene,[30] to temperatures above its melting point. The addition of nitric acid to an aqueous or ether solution of maleic acid produces the same results.[31] Terry and Eichelberger[32] reported that maleic acid, in aqueous solution, is transformed to fumaric acid by heating to 99.2° C. in the presence of hydrochloric or hydrobromic acid as catalysts. The reaction proceeds without the formation of by-products and its velocity is proportional to the concentration of the catalyst and to the second power of the original concentration of the maleic acid.

Both maleic and fumaric acids can be oxidized in aqueous solution to tartaric acid (racemic) by adding a solution of potassium permanganate at such a rate that the temperature does not rise above 50° to 60° C.[32a] On the other hand, in the presence of such acids as sulphuric, phosphoric, acetic and perchloric the principal product obtained on oxidation (with permanganate) is formic acid.[33]

PRODUCTION OF BENZALDEHYDE

Both benzaldehyde and benzoic acid can be produced by the oxidation of the same aromatic hydrocarbon, particularly toluene. In vapor phase oxidation the formation of one of these substances in predominance is dependent upon the conditions of oxidation, such as the rate of flow of the gases through the apparatus, the temperature, the quantity of air or other oxidizing gas, and the catalyst. Generally, high flow rates and a relatively low proportion of air or oxygen favor the production of the aldehyde.

Coquillion[34] obtained benzaldehyde as one of the oxidation products when a mixture of air and toluene vapor was passed over an incandescent platinum or palladium wire. Later Woog[35] used pumice impregnated with a reduced platinum salt, or the oxides of iron, nickel or copper at temperatures varying from 150° to 300° C. In the presence of manganese dioxide complete oxidation of the hydrocarbon was observed. Toluene was also oxidized at 370° C. in the presence of coke, yielding a small amount of benzaldehyde and a large proportion of benzoic acid. Woog considered that the best results were secured with the iron oxide catalyst. The reaction can be controlled by diluting the gaseous mixture with an inert gas, carbon dioxide or nitrogen.[36] Orloff[37] reported a

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[27] U. S. Patent 1,900,649, March 7, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, **27**, 2964.

[28] Witzel, U. S. Patent 1,900,680, March 7, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, **27**, 2965.

[29] Pelouze, *Ann.*, 1834, 11, 266; Tanatar, *Ann.*, 1893, **273**, 33; *Chem. Soc. Abs.*, 1893, **64** (1), 193; Skraup, *Monatshefte*, 1891, **12**, 117; *Chem. Soc. Abs.*, 1891, **60** (1), 1338; *Monatshefte*, 1893, **14**, 502; *Chem. Soc. Abs.*, 1894, **66** (1), 15.

[30] Tanatar, *Ann.*, 1893, **273**, 33; *Chem. Soc. Abs.*, 1893, **64** (1), 193; *Ber.*, 1894, **27**, 1366.

[31] Schmidt, *Ber.*, 1900, **33**, 3241.

[32] *J.A.C.S.*, 1925, **47**, 1402; see also Milas and Terry, *J.A.C.S.*, 1925, **47**, 1412.

[32a] Tanatar, *Ber.*, 1880, **13**, 1383; Kekulé and Anschütz, *Ber.*, 1881, **14**, 714.

[33] Hatcher and West, *Trans. Roy. Soc.*, 1927, (3) **21**, Sect. 3, 269; *Chem. Abs.*, 1928, **22**, 1518.

[34] *Compt. rend.*, 1873, **77**, 445; *Chem. Soc. Abs.*, 1873, **26**, 1214; *Compt. rend.*, 1875, **80**, 1089; *Chem. Zentr.*, 1875, 422.

[35] *Compt. rend.*, 1907, **145**, 124; *Chem. Soc. Abs.*, 1907, **92** (1), 753. Dennestedt and Hassler (German Patent 203,848, 1907; *J.S.C.I.*, 1908, **27**, 1223) suggested the use of coal, lignite or peat as catalysts for the oxidation of hydrocarbons, especially for the production of borneol and isoborneol. The addition of picric acid is said to increase the catalytic action of the carbonaceous materials.

[36] Chavy, Delage and Woog, French Patent *379,715*, *1907*; *J.S.C.I.*, 1907, **26**, 1254.

[37] *J. Russ. Phys.-Chem. Soc.*, 1908, **40**, 652; *Chem. Soc. Abs.*, 1908, **94** (1), 521.

2.5 to 4 per cent yield of benzaldehyde on passing a mixture of toluene vapor and air over heated copper. Other oxidation products, resembling phenols, were formed at the same time.

Kuznetzov and Stepanenko[38] investigated the following catalysts for the vapor phase oxidation of toluene to benzaldehyde: (1) basic zinc manganate, (2) vanadium pentoxide on asbestos, (3) vanadium pentoxide on pumice, (4) molybdenum trioxide on asbestos and (5) bismuth vanadate on pumice. The best catalyst was found to be molybdenum trioxide. The catalyst was preheated to 375° C., but after oxidation started the temperature rose to 475° C. Somewhat better yields were obtained using small pieces of molybdenum oxide (2 to 3 mm. in diameter) and keeping the temperature of the catalyst at 500° C. Under these conditions 42.3 per cent of the volatilized toluene was oxidized, of which 55.2 per cent was benzaldehyde, 5 per cent benzoic acid, and the remainder carbon dioxide. No carbon monoxide was formed.

Although vanadium pentoxide or vanadates appear to be excellent catalysts for the oxidation of aromatic compounds to acids, benzene to maleic acid or naphthalene to phthalic acid, for example, they do not favor good yields of benzaldehyde.[39] Meigs[40] noted when another metal, such as silver, was incorporated in the catalyst that larger proportions of benzaldehyde were obtained by the vapor phase oxidation of toluene. The temperature of the catalyst was kept at about 250° C., and steam was mixed with the reacting gases. The temperature and the quantity of steam were regulated so that the concentration of carbon dioxide in the exit gases was maintained at about 3 per cent. Good yields of benzaldehyde, however, are obtained by the use of vanadium pentoxide in the catalytic oxidation of benzyl alcohol or benzyl chloride with air.[41]

In the production of benzaldehyde by the catalytic oxidation of toluene vapors with air, Downs[42] controlled the temperature in the reaction zone by the vaporization of sulphur adjacent to but out of direct contact with the catalyst. The boiling point of the sulphur can be varied by changing the pressure on the system.

Several procedures have been developed for the liquid phase oxidation of toluene to benzaldehyde. One of these involves the use of manganese dioxide and sulphuric acid, the latter being in excess.[43] When 65 per cent sulphuric acid is employed, at 18° to 19° C., and the ratio of toluene to manganese dioxide is 4:1, the yield of benzaldehyde (calculated on the basis of the active MnO_2 content) is 55 to 56 per cent.[44] The addition of a small quantity of nitric acid accelerates the reaction, but cupric sulphate or potassium iodide are without effect.[45] Substitution of manganese dioxide by powdered pyrolusite, which had been previously treated with sodium hydroxide (10 to 25 per cent) in an autoclave at 156° to 158° C. under 6 to 6.5 atmospheres, reduced the proportion of aldehyde formed to about 14 per cent.

Other oxidizing agents include sulphuric acid solutions of manganese dioxysulphate[46] (prepared by the electrolysis of a solution of manganous sulphate) at 50° C. or of the ammonium manganic alum, $(NH_4)_2SO_4.Mn_2(SO_4)_3$. The addition of sulphuric acid slowly to a cooled mixture of lead dioxide, water and benzol also yields benzaldehyde.[47] A mixture of cerium dioxide in 60 per cent sulphuric acid at 90° C. is suggested[48] as well as ammonium persulphate in sulphuric acid (containing a small proportion of silver sulphate), at room temperature.[49] Oxidation of toluene with chromyl chloride furnishes the compound $C_6H_5CH(CrOCl_2.OH)_2$ which on hydrolysis gives benzaldehyde. The reaction may be carried out in either carbon bisulphide[50] or chloroform[51] solutions.

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[38] *Ukrainskii Khem. Zhur.*, 1929, **4**, (Tech. Pt.), 153; *Chem. Abs.*, 1930, **24**, 2434.

[39] Shorigin, Kizberg, Troitski and Smolyaninova, *J. Chem. Ind. Moscow,* 1929, **6**, 258; *Brit. Chem. Abs.* **B**, 1929, 934.

[40] U. S. Patent 1,560,297, Nov. 3, 1925; assigned to Ellis-Foster Co.

[41] Shorigin, Kizberg, Troitski and Smolyaninova, *loc. cit.*

[42] U. S. Patent 1,589,632, June 22, 1926; *Chem. Abs.*, 1926, **20**, 3015.

[43] Soc. chim. des usines du Rhône anciennement Gilliard, Monnet et Cartier, German Patent 101,221, 1897; *Chem. Zentr.*, 1897, **1**, 959; German Patent 107,722, 1898; *Chem. Zentr.*, 1900, **1**, 1113. Law and Perkin, *J.C.S.*, 1907, **91**, 261. *Cf.* Kaminskii, Russian Patent 58,1924; *Chem. Abs.*, 1933, **27**, 3942.

[44] Shorigin, Kizberg, Troitski and Smolyaninova, *loc. cit.*

[45] The use of cupric sulphate ($CuSO_4.H_2O$) as a catalyst is described by Evdokimov, *J. Chem. Ind. (Russia)*, 1929, **6**, 207; *Chem. Abs.*, 1930, **24**, 2737.

Toluene can be oxidized indirectly to benzaldehyde. For instance, benzyl chloride (obtained by chlorinating toluene) is hydrolyzed to benzyl alcohol by refluxing with a solution of sodium hydroxide for several hours. The reaction product is treated with aqueous sodium hypochlorite, containing 2 to 3 per cent sodium hydroxide. During the addition of the hypochlorite, the benzaldehyde formed is separated by steam distillation.[52]

Aldehydes can be obtained directly from aromatic hydrocarbons by treating them with carbon monoxide and hydrogen chloride in the presence of aluminum chloride.[53] To illustrate, carbon monoxide and hydrogen chloride are passed for 6 to 8 hours into a solution of benzene in nitrobenzene to which aluminum chloride is added. During passage of the gases a temperature of 50° to 60° C. is maintained. The reaction product is poured onto ice, and benzene, benzaldehyde and nitrobenzene are separated by steam distillation. The benzaldehyde can be further purified by converting it to its bisulphite compound. This method is applicable not only to the production of substituted aldehydes, such as chlorobenzaldehyde or p-toluic aldehyde, but to the preparation of chlorine-free aldehydes which can be used in the manufacture of perfumes and preservatives.

When dissolved in glacial acetic acid saturated with nitrous oxides (N_2O_3) and exposed to light or heated to 120° C., toluene yields a mixture of benzaldehyde, benzoic acid, and a small proportion of unidentified nitrated products.[54] Benzaldehyde and benzoic acid are separated from the mixture by treatment with a concentrated solution of sodium bisulphite and a dilute solution of sodium hydroxide, respectively. Similar results were obtained when nitrogen tetroxide was used as the oxidizing agent. The reactions involved may be represented by:

$$C_6H_5CH_3 + N_2O_3 \longrightarrow C_6H_5COOH + H_2O + N_2$$
$$2C_6H_5CH_3 + N_2O_4 \longrightarrow 2C_6H_5CHO + 2H_2O + N_2$$

One of the characteristic reactions of benzaldehyde is its autoxidation, particularly in the presence of sunlight. This apparently takes place in two stages: (1) the formation of perbenzoic acid from benzaldehyde, and (2) the oxidation of benzaldehyde to benzoic acid by the perbenzoic acid.

$$C_6H_5CHO + O_2 \longrightarrow C_6H_5COOOH$$
$$C_6H_5COOOH + C_6H_5CHO \longrightarrow 2C_6H_5COOH$$

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[46] Badische Anilin- und Soda-Fabrik, German Patent 175,295, 1903; *Chem. Zentr.*, 1906, **2**, 1589. *Cf.* Lang, German Patent 189,178, 1902; *Chem. Abs.*, 1908, **2**, 1209.

[47] Law and Perkin, *J.C.S.*, 1907, **91**, 261.

[48] Farbwerke vorm Meister, Lucius und Brüning, German Patent 158,609, 1902; *Chem. Zentr.*, 1905, **1**, 840.

[49] Law and Perkin, *loc. cit.*

[50] Étard, *Ann. chim. phys.*, 1881, (5) **22**, 225; *Chem. Soc. Abs.*, 1881, **40**, 581; Bornemann, *Ber.*, 1884, **17**, 1464.

[51] Law and Perkin, *loc. cit.*

[52] Benedetti, Vanselow and Vanselow, U. S. Patent 1,405,261, Jan. 31, 1922; *Chem. Abs.*, 1922, **16**, 1781.

[53] Schütz, German Patent 403,489, 1921; *J.S.C.I.*, 1925, **44**, 378B; assigned to Gelsenkirchener Bergwerks A.-G. The action of carbon monoxide on aromatic hydrocarbons has been extended to hydroaromatics, such as hexahydrotoluene and cyclohexane; I. G. Farbenindustrie A.-G., German Patent 520,154, 1927; *Chem. Abs.*, 1931, **25**, 3664.

[54] Giacalone, *Gazz. chim. ital.*; 1931, **61**, 828; *Chem. Abs.*, 1932, **26**, 1910.

These reactions can be accelerated, particularly when the aldehyde is dissolved in a solvent, by the presence of iron powder. Tin and aluminum powders, however, have no effect. Perbenzoic acid may be isolated from an acetone solution by distilling off the acetone, or by extracting the benzoic acid with dilute sulphuric acid followed by extraction with chloroform.[55] When dissolved in pyridine, benzaldehyde fails to exhibit autoxidation.

PRODUCTION OF BENZOIC ACID

In making benzoic acid by the vapor phase oxidation of toluene, Kuznetzov and Stepanenko[56] used a large excess of air, stannic vanadate as the catalyst, and a temperature of 290° C. About 21 per cent of the vaporized toluene was oxidized, the products consisting of 87.9 per cent benzoic acid and 7 per cent benzaldehyde.

Maxted[57] reported that stannic vanadate can be used in the vapor phase oxidation of toluene and ethylbenzene to benzoic acid. With the former a 50 per cent yield was obtained, and with the latter, a 40 per cent yield. The same catalyst can be employed in the oxidation of benzyl alcohol and benzaldehyde to benzoic acid. Bismuth vanadate yielded results similar to those with the tin compound though the temperature of activity is about 100° C. higher (about 390° C.). Pansegrau[57a] employed hydrated ferric oxide at 150° C. as a catalyst for the conversion of toluene to benzoic acid under pressure in the presence of a liquid aqueous phase.

Other methods for the catalytic oxidation of toluene to benzoic acid involve the use of a zeolite catalyst[58] containing vanadium, tungsten and molybdenum; the spraying of a colloidal solution of vanadium oxide in toluene[59] together with eight times its vapor volume of air into a chamber kept at 200° to 300° C.; and the oxidation of naphthalene in the presence of a relatively large quantity of steam (see Phthalic Acid).

This acid can be made also by heating solutions of phthalic acid or of phthalates to 150° to 300° C. under pressure,[60] or by heating a mixture of solid calcium phthalate and calcium hydroxide.[61]

Several procedures are available for the recovery of benzoic acid from phthalic acid made by the oxidation of naphthalene. The aqueous solution, or dispersion, of these two acids can be continuously leached with a current of an organic solvent, such as gasoline or benzene, in which the benzoic acid is the more soluble.[62] Benzoic is recovered from this solvent and phthalic acid from the water. Mixtures of benzoic and phthalic acids may be treated with the vapors of an organic solvent for benzoic acid at temperatures at which the latter acid is volatile (125° to 150° C.) but below those at which phthalic acid is transformed into the anhydride.[63] This operation can be carried out in the presence of steam and made continuous.

[55] Van der Beek, *Rec. trav. chim.*, 1928, **47**, 286; *Brit. Chem. Abs.* **A**, 1928, 413.

[56] *Loc. cit.*

[57] *J.S.C.I.*, 1928, **47**, 101T.

[57a] U. S. Patent 1,815,985, July 28, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 5432.

[58] Jaeger, U. S. Patent 1,694,122, Dec. 4, 1928; assigned to Selden Co.; *Chem. Abs.*, 1929, **23**, 850.

[59] Caspari, British Patent 263,201, 1925; *Brit. Chem. Abs.* **B**, 1927, 378; U. S. Patent 1,674,589, June 19, 1928; *Chem. Abs.*, 1928, **22**, 2756.

[60] Daudt, U. S. Patent 1,551,373, Aug. 25, 1925; *Chem. Abs.*, 1926, **20**, 51.

[61] Fairweather, Beckett and Thomas, U. S. Patent 1,727,102, Sept. 3, 1929; assigned to Selden Co.; *Chem. Abs.*, 1929, **23**, 5196.

[62] Jaeger, U. S. Patent 1,685,634, Sept. 25, 1928; assigned to Selden Co.; *Chem. Abs.*, 1928, **22**, 4539.

[63] Jaeger, U. S. Patent 1,694,124, Dec. 4, 1928; assigned to Selden Co.; *Chem. Abs.*, 1929, **23**, 849.

The mixture of acids can also be subjected to the action of superheated steam at temperatures (150° to 175° C.) below which phthalic anhydride is formed. The vapors of steam and benzoic acid are partially condensed and benzoic acid recovered.[64]

Although both the liquid- and vapor-phase oxidation of toluene at ordinary pressures gives mainly benzaldehyde and benzoic acid, Newitt and Szegö[64a] observed that at 50 atmospheres and 210° C., toluene is oxidized by air to hydroxylated compounds, of which benzyl alcohol is the chief product. Small amounts of 2,4-dihydroxytoluene, benzaldehyde and benzoic acid are also formed.

PRODUCTION OF PHTHALIC ACID

Phthalic anhydride, from which phthalic acid can be obtained, is easily produced at a low cost by catalytic oxidation of naphthalene with air. It is an important raw material in the manufacture of anthraquinone or vat dyes and also of synthetic resins.[64b] Esters of this acid are used as plasticizers.

The catalysts most extensively employed in the oxidation of naphthalene are vanadium pentoxide or vanadates. When the vapors of naphthalene or alkylnaphthalenes (e.g., methylnaphthalene) together with air are conducted over vanadium pentoxide at 450° C. about 87 per cent of the hydrocarbon is converted to phthalic anhydride.[65] Other compounds produced at the same time are benzoic acid, carbon dioxide and possibly naphthols. Buylla and Pertierra[65a] observed that o-xylene under similar conditions also yielded phthalic anhydride. The catalyst is best prepared by fusing vanadium pentoxide and then reducing it to a powder. Arsenic trioxide and sulphur dioxide do not affect the catalyst. Sodium salts, however, greatly lower its efficiency. Molybdenum can be used as a catalyst, though it is not as efficient as vanadium pentoxide. The oxidation of naphthalene with air takes place also in the presence of zeolites[66] as well as the vanadates of tin and bismuth.[67] The catalysts may be supported on a smooth or polished metal carrier. For example, a catalyst is prepared by immersing small polished strips of aluminum into molten vanadium pentoxide.[68]

Kusama[69] found that acidic oxides were the best promoters for vanadium pentoxide catalysts, as the basic oxides, including the lower oxides of vanadium, combine with the acid which is produced. He also noted that the presence of water vapor increased the yield of benzoic acid. The addition of steam has been reported by Conover,[70] who obtained a 90 per cent yield of benzoic acid by passing phthalic anhydride vapors and steam over catalysts of zinc, copper or aluminum oxide at 200° to 600° C. Phthalic acid, together with maleic acid, carbon dioxide and water, is obtained by the catalytic oxidation of hydro-aromatic compounds, such as decahydronaphthalene.[71]

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[64] Jaeger, U. S. Patent 1,686,913, Oct. 9, 1928; assigned to Selden Co.; *Chem. Abs.*, 1928, 22, 4539.

[64a] *Chem. and Ind.*, 1933, 645; *Chem. Abs.*, 1933, 27, 5064.

[64b] See Ellis, *Ind. Eng. Chem.*, 1933, 25, 125; *ibid.*, 1934, 26, 37; "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York. Uses of maleic acid and phthalic anhydride are discussed by Downs, *Ind. Eng. Chem.*, 1934, 26, 17.

[65] Conover and Gibbs, *Ind. Eng. Chem.*, 1922, 14, 120. Gibbs, U. S. Patent 1,591,619, July 6, 1926; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1926, 20, 3171. *Cf.* Buylla and Pertierra, *Anal. soc. espan. fis. quim.*, 1933, 31, 59; *Brit. Chem. Abs.* **A**, 1933, 943.

[65a] *Loc. cit.*

[66] Jaeger, U. S. Patent 1,692,126, Nov. 20, 1928; U. S. Patents 1,844,387 and 1,844,388, Feb. 9, 1932. *Chem. Abs.*, 1932, 26, 1947; all patents assigned to Selden Co.

[67] Maxted and Coke, British Patent 228,771, 1924; *J.S.C.I.*, 1925, 44, 279B.

[68] Verein für chemische und metallurgische Produktion, German Patent 478,192, 1924; *Chem. Abs.*, 1929, 23, 4231. *Cf.* Compagnie nationale de matières colorantes et manuf. de produits chim. du nord réunies établissements Kuhlmann, French Patent 646,264, 1927; *Chem. Abs.*, 1929, 23, 2078.

[69] *Bull. Inst. Phys. Chem. Research* (*Tokyo*), 7, 1087; *Abs. sect.*, 1928, 1, 105; *Chem. Abs.*, 1929, 23, 3621.

[70] U. S. Patent 1,645,180, Oct. 11, 1927; assigned to Monsanto Chemical Works; *Brit. Chem. Abs.* **B**, 1928, 117.

Catalytic processes of the kind described above, e.g., the conversion of benzene to maleic acid or naphthalene to phthalic anhydride, depend for their success on the accurate control of temperature. For such control a number of methods have been developed, several of which have already been mentioned.

Downs,[72] for example, immersed the reaction vessel in a eutectic mixture of sodium and potassium nitrates to maintain a constant temperature. The catalyst was coated directly on the walls of the vessel. This mixture of nitrates and a large number of small reaction chambers has been employed by Gibbs.[73]

As heat absorbents, alloys of mercury, cadmium and lead can be used.[74] These three metals are mixed in various proportions to obtain alloys which boil over a wide range of temperatures. Using mercury alone presents some disadvantages, since its boiling point is low, its cost high, and it has a relatively low heat conductivity. Alloys formed from these three metals have low melting points, sufficiently high boiling points, high thermal capacities, and relatively low specific gravities. Various details of apparatus for controlling the temperature have also been described by Jaeger[74a] and Selden.[74b]

Green[75] suggested that the surplus heat generated during the oxidation reactions be absorbed by the injection of a water spray into the spaces between the successive catalyst zones. The evaporation of the water by the hot gases thus reduces their temperature.

Temperature control is also obtained by allowing oxidation to proceed in steps. The gases are first passed over a less active catalyst at a moderate temperature and then over a more active catalyst.[76] The heat of reaction from the first step thus heats the gases to an appropriate temperature for the second step. For example, naphthalene vapors and air are led first over vanadic acid on metallic granules at 320° C. and then over vanadic acid on powdered kieselguhr at 350° to 410° C.

Crude phthalic anhydride can be purified in several ways. The reaction products coming directly from the reaction chamber are brought into contact with large surfaces of solid adsorbents (e.g., silica gel or pumice) which are maintained at a temperature low enough to prevent decomposition of the reaction products.[77] Granulated pumice or bauxite have been suggested for the removal of impurities in a similar manner.[78] In another process the crude solid anhydride is vaporized into a current of air or purified flue gas at a temperature of about 200° C. The gaseous mixture is cooled in successive stages to fractionally crystallize the vaporized substances.[79] The crude acid or anhydride may be freed of impurities by selective steam distillation at temperatures below which the acid distills.[80]

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[71] Shimose, *loc. cit.*

[72] *J.S.C.I.*, 1926. **45**, 188T. U. S. Patent 1,604,739, Oct. 26, 1926; assigned to The Barrett Co.; *Brit. Chem. Abs.* **B**, 1927, 60.

[73] U. S. Patent 1,599,228, Sept. 7, 1926; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1926, **20**, 3460. Also British Patent 275,321, 1926; *Brit. Chem. Abs.* **B**, 1927, 772.

[74] Canon and Andrews, U. S. Patent 1,689,860, Oct. 30, 1928; assigned to Selden Co.; *Chem. Abs.*, 1929, **23**, 156. See also, U. S. Patent 1,735,951, Nov. 19, 1929, and British Patent 282,559, 1927; both patents assigned to Selden Co.; *Chem. Abs.*, 1930, **24**, 670; *ibid.*, 1928, **22**, 3714.

[74a] U. S. Patent 1,685,672, Sept. 25, 1928; *Brit. Chem. Abs.* **B**, 1929, 229; U. S. Patent 1,812,341, June 30, 1931; *Chem. Abs.*, 1931, **25**, 5016; British Patent 306,519, 1928; *Brit. Chem. Abs.* **B**, 1929, 628; British Patent 310,956, 1929; *Brit. Chem. Abs.* **B**, 1930, 493; all patents assigned to Selden Co.

[74b] U. S. Patent 1,647,317, Nov. 1, 1927; *Chem. Abs.*, 1928, **22**, 242.

[75] British Patent 249,973, 1925; *Chem. Abs.*, 1927, **21**, 1007.

[76] I. G. Farbenindustrie A.-G., German Patent 441,163, 1922; *Brit. Chem. Abs.* **B**, 1927, 903.

[77] I. G. Farbenindustrie A.-G., British Patent 272,557, 1926; *Brit. Chem. Abs.* **B**, 1928, 440.

[78] Brode and Johannsen, U. S. Patent 1,693,915, Dec. 4, 1928; assigned to Grasselli Dyestuff Corp.; *Chem. Abs.*, 1929, **23**, 845. See also Brode and Johannsen, U. S. Patent 1,889,945; Dec. 6, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 1642.

[79] Andrews, U. S. Patent 1,685,624, Sept. 25, 1928; assigned to Selden Co.; *Chem. Abs.*, 1928, **22**, 4539.

The crude product can also be treated in the solid or liquid phase with reagents which react with the impurities and afterwards the phthalic acid is separated by distillation. These reagents may be condensing agents, for example, manganese dioxide or zinc chloride,[81] an aldehydic material such as trioxymethylene,[82] acid compounds, e.g., sulphuric acid,[83] lactic, mucic, or citric acid[83a] or sodium acid sulphate,[84] or the impurities may be selectively chlorinated to form high-boiling substances.[85] The crude acid is also purified by distillation followed by extraction with toluene or xylene or mixtures of these solvents.[86]

The decarboxylation of phthalic acid to yield benzoic acid has been effected by subjecting the vapors to the influence of splitting catalysts[86a] and to electronic discharges.[86b]

PRODUCTION OF ANTHRAQUINONE

Anthraquinone is of commercial importance because of its use in the preparation of dyes, particularly alizarin, quinizarin and purpurin. One of the earliest methods of preparation on a commercial scale was the oxidation of anthracene by potassium dichromate and sulphuric acid.[87]

Anthraquinone is now, however, produced by the vapor phase catalytic oxidation of anthracene. Thus, Jaeger[88] oxidized anthracene with air in the presence of a zeolite catalyst at 400° to 500° C. Canon and Andrews[89] used molybdenum trioxide at 450° to 550° C. and kept the temperature constant by removing the excess heat generated by means of a cooling medium consisting of an alloy of cadmium and mercury.

Wohl[89a] oxidized anthracene to anthraquinone by passing a mixture of air and anthracene over a vanadium oxide catalyst supported on pumice at about 400° C. Triphenylmethane also yielded anthraquinone, whereas toluene produced benzaldehyde and benzoic acid. Tar fractions containing aralkyl hydrocarbons were found to give a mixture of aldehydes and acids. Unsaturated hydrocarbons of high molecular weight such as those which occur in brown-coal tar were similarly converted to acids.

[80] Jaeger, U. S. Patent 1,892,396, Dec. 27, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, **27**, 1895; U. S. Patent 1,889,961, Dec. 6, 1932; assigned to Selden Research and Engineering Corp.; *Chem. Abs.*, 1933, **27**, 1640.

[81] Bowers, U. S. Patent 1,728,225, Sept. 17, 1929; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1929, **23**, 5196.

[82] Conover, U. S. Patent 1,755,242, April 22, 1930; assigned to Monsanto Chemical Works; *Chem. Abs.*, 1930, **24**, 2760.

[83] Foster, U. S. Patent 1,817,304, Aug. 4, 1931; assigned to National Aniline and Chemical Co., Inc.; *Brit. Chem. Abs.* **B**, 1933, 219.

[83a] Conover, U. S. Patent 1,916,657, July 4, 1933; assigned to Monsanto Chemical Co.; *Chem. Abs.*, 1933, **27**, 4545.

[84] Bowers, U. S. Patent 1,897,110, Feb. 14, 1933; assigned to E. I. duPont de Nemours and Co., Inc.; *Chem. Abs.*, 1933, **27**, 2695.

[85] Jaeger and Canon, U. S. Patent 1,702,871, Feb. 19, 1929; *Chem. Abs.*, 1929, **23**, 1650; Jaeger, British Patent 285,017, 1928; *Brit. Chem. Abs.* **B**, 1929, 672; both patents assigned to Selden Co. See also French Patent 647,880, 1928; *Chem. Abs.*, 1929, **23**, 2449.

[86] Compagnie nationale de matières colorantes et manuf. de produits chim. du nord réunies établissements Kuhlmann, French Patent 648,163, 1927; *Chem. Abs.*, 1929, **23**, 2724.

[86a] Jaeger, U. S. Patent 1,892,766, Jan. 3, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, **27**, 2160.

[86b] Jaeger, U. S. Patent 1,909,357, May 16, 1933; assigned to Selden Co., *Chem. Abs.*, 1933, **27**, 3671.

[87] Levinstein, *J.S.C.I.*, 1883, **2**, 219. Kopp, *Jahresberichte*, 1878, 1188.

[88] U. S. Patent 1,685,635, Sept. 25, 1928; *Brit. Chem. Abs.* **B**, 1929, 200. Jaeger and Pietzsch, U. S. Patent 1,849,833, Mar. 15, 1932; assigned to Selden Research and Engineering Corp.; *Chem. Abs.*, 1932, **26**, 2748.

[89] U. S. Patent 1,614,185, Jan. 11, 1927; *Chem. Abs.*, 1927, **21**, 745; Reissue 16,824, Dec. 20, 1927.

[89a] U. S. Patents 1,787,416 and 1,787,417, Dec. 30, 1930 (application date in Germany, June 22, 1916); assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 716.

Craver[90] concluded that the oxides of vanadium were too energetic as catalysts and with them phthalic anhydride was the main product in the oxidation of anthracene. The oxides of molybdenum, uranium, or other metals of the fifth and sixth groups in the periodic system were more satisfactory. Best results were obtained by using a mixture of such oxides. The optimum temperature for oxidation is about 475° C. and the time of contact of the gases with the catalyst about 0.5 second.

Instead of using air alone, the oxides of nitrogen together with air furnish a convenient oxidizing gas. In one process these oxides are absorbed by basic oxides, such as zinc or copper oxide, and the resulting compounds mixed with anthracene. The mixture is heated to 250° to 350° C. and a stream of air passed through the mass. In this manner anthracene is oxidized to anthraquinone.[91]

Nitrogen oxides may be dissolved in nitrobenzene and anthracene added slowly to the solution. After standing for some time the excess oxides are removed by heating to 100° C. On cooling the nitrobenzene, crystals of anthraquinone separate and are freed of the solvent by filtration. Additional anthraquinone is obtained by steam distillation of the nitrobenzene. This method of oxidation is not applicable to anthracene containing a large proportion of impurities, as it is difficult to separate anthraquinone from other substances formed on oxidation.[92]

Small quantities of anthraquinone have also been obtained in the oxidation of toluene vapor, or the vapor of toluene-containing petroleum distillates, using a catalyst consisting of aluminum grains coated with vanadium pentoxide,[93] at a temperature of 400° C.

OXIDATION IN THE LIQUID PHASE

Oxidation of aromatic hydrocarbons can be carried out in the liquid phase as well as in the vapor phase. In the preparation of phenol, benzene is emulsified with an equal volume of 20 per cent sodium hydroxide solution and this emulsion is heated in an autoclave at 320° to 400° C. for one hour, an internal pressure of about 200 atmospheres being maintained.[94] The oxides of uranium, together with the oxides of molybdenum, vanadium or tungsten, are used as catalysts. The oxygen in the air above the liquid in the autoclave is absorbed with the formation of phenol, which dissolves in the alkali. The yield of phenol is small. Amiel[94a] heated 1 mole of benzene with 15 gram-atoms of oxygen at 460° to 490° C. for periods ranging from 1.4 to 2 hours. The maximum yield of phenol was 4.5 milligrams from 25 milligrams of benzene. At the same time, 1.7 milligrams of 1,4-benzoquinone were formed.

Aromatic hydrocarbons with side chains, when heated in an autoclave with air or oxygen under high pressure (60 atmospheres) in the presence of a solution of alkalies produce acids or aldehydes.[95] Good stirring during heating promotes emulsification which, in turn, facilitates oxidation. High temperatures and long reaction periods, however, favor the formation of acids. Aldehydes require lower temperatures and shorter reaction periods and also continuous removal of the hydrocarbon, in which the aldehyde is soluble. Compounds which are oxygen carriers may be used as catalysts.

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[90] U. S. Patent 1,636,856, July 26. 1927; assigned to Barrett Co.

[91] Chem. Fabr. Grünau, Landshoff and Meyer A.-G., German Patent 215,335, 1908; *J.S.C.I.*, 1909, **28**, 1310.

[92] Iljinski, Maksorov and Elagin, *J. Chem. Ind. (Moscow)*, 1928, **5**, 469; *Chem. Abs.*, 1928, **22**, 3888. For purification of anthracene by selective catalytic oxidation and selective solvent action of furfural see Jaeger, *Ind. Eng. Chem.*, 1928, **20**, 1330; U. S. Patent 1,920,796, Aug. 1, 1933; assigned to Selden Co.; *Chem. Abs.*, 1933, **27**, 4813.

[93] Bowen and Nash. *J. Inst. Pet. Tech.*, 1928, **14**, 106.

[94] Hale, U. S. Patent 1,595,299, Aug. 10, 1926; assigned to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1926, 910.

[94a] *Compt. rend.*, 1933, **196**, 1896; *Chem. Abs.*, 1933, **27**, 4530. *Cf.* Amiel, *Compt. rend.*, 1933, **196**, 1122; *Brit. Chem. Abs.* **A**, 1933, 600; Newitt and Szegö, *Chem. and Ind.*, 1933, 645.

[95] Fischer, German Patent 364,442, 1919; *J.S.C.I.*, 1923, **42**, 576A.

Alkylbenzenes having a side chain of two or more carbon atoms can be oxidized in the liquid phase with air or oxygen in the presence of catalysts such as the oxides or hydroxides of silver, copper, zinc and other metals, or the acetates, stearates or resinates of iron and manganese.[96] The temperature varies with the hydrocarbon being treated, the range generally being from about 50° C. to the boiling point of the hydrocarbon. As an example of the products obtained by this process, ethylbenzene at 120° to 140° C. is oxidized to a mixture of acetophenone and methylphenylcarbinol.

The oxidation of ethylbenzene in the liquid phase has been studied by Stephens [96a] and King, Swann and Keyes.[96b] The best yield of acetophenone was obtained with manganese acetate as catalyst, although acetic anhydride and to some extent, cerium oxide, also accelerated the oxidation.

Senseman and Stubbs [96c] investigated both the vapor- and liquid-phase oxidation of p-cymene. Vanadium pentoxide supported on porcelain was employed at 300° to 400° C. as a catalyst for the vapor-phase and manganese dioxide at 140° to 160° C. for the liquid-phase oxidation. The products in either case were p-toluic acid, terephthalic acid, acetic acid, formaldehyde, carbon dioxide and water. p-Tolyl methyl ketone was also found in the liquid-phase reaction products. Senseman and Stubbs [96d] also carried out the liquid-phase oxidation of ethylbenzene at temperatures of 102° to 104° C. in the presence of manganese dioxide. Acetophenone, benzoic acid, phenylmethylcarbinol, formaldehyde, carbon dioxide and water resulted.

Oxygenated products of hydroaromatic compounds are made by oxidation at relatively low temperatures in the presence of mild catalytic agents. Thus, α-ketotetrahydronaphthalene and other oxidation products are obtained at temperatures below 130° C. with oxygen or other oxidizing agents with catalysts such as the salts or oxides of manganese or copper.[97]

Aromatic hydrocarbons are oxidized with oxygen under the influence of light in the presence of anthraquinone or chloroanthraquinones.[98] By the addition of acetic anhydride, or acetyl chloride or other substances which react with the final or intermediate oxidation products, derivatives of the oxidation products, such as esters, can be obtained directly.

In the oxidation of aromatic alcohols with gaseous oxygen Stephens [99] noted that three reactions appear to take place: (1) a small proportion of the alcohol is oxidized directly to ketones; (2) high-boiling compounds are formed which correspond to two molecules of the alcohol less one molecule of water, this reaction taking place to the largest extent; and (3) the formation of unsaturated compounds by dehydration. All three of these reactions are completely inhibited by the presence of excess water. The alcohols used in this investigation were methylphenylcarbinol, ethylphenylcarbinol, dimethylphenylcarbinol and others of a similar type.

[96] I. G. Farbenindustrie A.-G., British Patent 309,005, 1927; *Brit. Chem. Abs.* **B**, 1929, 917. See also French Patent 676,826, 1929; *Chem. Abs.*, 1930, **24**, 3022.

[96a] *J.A.C.S.*, 1926, **28**, 1824; *ibid.*, 1926, **48**, 2920; *ibid.*, 1928, **50**, 2523.

[96b] *Ind. Eng. Chem.*, 1929, **21**, 1227.

[96c] *Ind. Eng. Chem.*, 1931, **23**, 1129, *ibid.*, 1932, **24**, 1184.

[96d] *Ind. Eng. Chem.*, 1933, **25**, 1286.

[97] Hess and Felser, German Patent 520,290, 1925; assigned to J. D. Riedel-E.de Haën A.-G.; *Chem. Abs.*, 1931, **25**, 2740.

[98] Eckert, British Patent 182,487, 1922; *Chem. Abs.*, 1922, **16**, 4214.

[99] *J.A.C.S.*, 1928, **50**, 186. See also Nozicka, British Patent 354,096, 1930; assigned to Kreidl, Rosen and Rutter, (Verein. Chem. Fabr. Kreidl, Heller & Co.); *Brit. Chem. Abs.* **B**, 1931, 1133.

ELECTROCHEMICAL OXIDATION

Many attempts have been made to utilize the electric current as the oxidizing agent for the commercial preparation of organic compounds. Although this has been done successfully in a number of processes, nevertheless, in many others the results have been disappointing because of low yields and the difficulty of regulating the oxidizing action. A great many organic compounds are oxidized completely in this manner, to yield carbon dioxide and water. Some of the factors regulating these electrolytic oxidation processes have been pointed out by Fichter.[100]

Aromatic hydrocarbons such as benzene are insoluble in aqueous solutions and are non-conductors. They must, therefore, be vigorously stirred with solutions to form exceedingly fine emulsions, which behave like true solutions. The final oxidation product then depends upon the construction of the apparatus, the type of electrodes used, and the choice of the electrolyte. These points can be illustrated by the following brief description of the conditions for the oxidation of benzene.

The construction of the apparatus.—With a platinum electrode and a cell which contains a diaphragm, benzoquinone is obtained, but in the absence of the diaphragm, quinol is formed.

The type of electrode.—The most vigorous oxidation is obtained with smooth electrodes. Peroxidized lead electrodes are next in order of activity. Graphite can be used, but it disintegrates mechanically, and also absorbs the organic substances. Electrodes in operation often become hot and may produce undesirable changes in the organic materials.

The type of electrolyte.—Dilute sulphuric acid is most generally used. It has been suggested that with this electrolyte the reaction is an indirect electrochemical oxidation as the acid is oxidized to persulphuric acid which is then reduced by the organic substance. This may also apply to the use of salts of metals possessing more than one valence state, such as chromium, manganese, or vanadium. Alkaline solutions often yield products entirely different from those obtained in acid solutions. Thus, the electrochemical oxidation of benzene in an alkaline solution does not yield quinones, not because they are not formed but because in alkaline solutions quinones are unstable and are immediately oxidized to hydroxyquinone-like substances.

Anodic oxygen, however, is the strongest of all oxidizing agents. It attacks benzene and its homologues directly in the nucleus, changing them into phenols and quinones. It can also effect the linking together of two molecules by eliminating one atom of hydrogen from each. In addition side-chains are attacked, forming aldehydes and oxides. The latter substances themselves can be further transformed into hydroxy-acids, which in turn can undergo degradation.

Several procedures for the electrolytic oxidation of aromatic compounds have been proposed. Mann and Paulson[101] found that toluene could be oxidized to benzaldehyde by the electrolysis of toluene-acetic acid-nitric acid mixtures. The highest yield was 19 per cent. A diaphragm and electrodes of sheet platinum were used. Acetone, alcohol, and carbon tetrachloride were found to be unsatisfactory as solvents and the principal objection to ether was its low boiling point. The reaction is distinctly electrochemical, since experiments carried out under identical conditions but without the applied electromotive force yielded no traces of benzaldehyde.

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[100] *J.S.C.I.*, 1929, **48**, 325T, 341T. *J. chim. phys.*, 1926, **23**, 481; *Brit. Chem. Abs.* **A**, 1926, 912. The electrolytic oxidation of alcohols, aromatic amines and phenols has been studied by Marie and Lejeune (*Compt. rend.*, 1928, **187**, 343; *Chem. Abs.*, 1928, **22**, 4345; *J. chim. phys.*, 1929, **26**, 237; *Chem. Abs.*, 1929, **23**, 4411).

[101] *Trans. Amer. Electrochem. Soc.*, 1925, **47**, 101; *Chem. Abs.*, 1925, **19**, 783.

Both the indirect and direct oxidation of toluene has been investigated by Mitchell.[102] In the former method toluene was first sulphonated to p-toluenesulphonic acid. The electrolysis of a 40 per cent aqueous solution of this acid at 100° C. yielded p-sulphobenzoic acid in quantities equivalent to 21.8 per cent current efficiency. An anode of lead wool was used. In the direct method, with an emulsion of toluene and a solution of 2N sulphuric acid or sodium hydroxide, practically no oxidation took place. The addition of various emulsifying agents did not help. However, when the toluene was emulsified with 55 per cent sulphuric acid containing manganous sulphate, at a temperature of 55° C., and using sheet lead electrodes, benzaldehyde was produced at a current efficiency of 61 per cent in a continuous system. With chromic sulphate under the same conditions benzoic acid was produced with an efficiency as high as 54 per cent. In these two latter treatments the toluene is oxidized by the manganic sulphate or chromic acid, which are the primary anodic oxidation products. A certain amount of cresol is also produced by the direct anodic oxidation of toluene.

The electrochemical oxidation of xylene yields a variety of products depending upon the conditions during electrolysis.[103] Using a lead oxide anode, a lead cathode, and a diaphragm, the oxidation of toluene suspended in 0.5N sulphuric acid yielded p-toluic acid and aldehyde, p-xylenol, p-xyloquinol and p-xyloquinone. Without a diaphragm the products were about 70 per cent p-hydrotoluoin, 10 per cent iso-p-hydrotoluoin, and some p-tolylmethyl alcohol. Suspending the xylene in a mixture of acetone and 2N sulphuric acid the oxidation products were p-tolualdehyde, a trace of terephthalic acid, and a small quantity of ω-acetylstyrene-p-carboxylic acid. The latter compound was formed by the condensation of acetone with the terephthalic acid formed by the electrochemical oxidation.

Anthracene, suspended in dilute sulphuric acid, is oxidized only to a very slight extent even at 80° C. The use of ceric sulphate as a catalyst increases the current efficiency to only 8 to 9 per cent. With the type of anode developed by Rasch and Lowy,[104] however, a current efficiency of over 26 per cent was obtained. This type of electrode is prepared by inserting a paste of a finely ground mixture of anthracene and lead peroxide (1 : 3) with dilute sulphuric acid into the openings of the grid plate of a lead accumulator, after the grid has been superficially oxidized with nitric acid. This grid is then used as the anode in an electrolytic cell containing dilute sulphuric acid. The addition of ceric sulphate to the sulphuric acid increased the current efficiency to over 40 per cent with this anode.

For the electrochemical oxidation of anthracene and other organic compounds Field[105] suggested a catalyst made from Swedish cerite ore. The ore is treated with concentrated sulphuric acid at 200° C., and then with cold water. The precipitate formed on the addition of oxalic acid, or sodium hydroxide, and which contains metals of the rare earth type, is used as a catalyst.

MISCELLANEOUS OXIDATION REACTIONS

The catalytic oxidation of the nitro and halogen derivatives of toluene proceeds in about the same manner as the oxidation of toluene itself.[106] Thus, in the oxidation of p-nitrotoluene with air at 270° to 300° C. in the presence of granulated tin vanadate as a catalyst a 14 to 16 per cent yield of p-nitrobenzoic acid was obtained. Under the same conditions o-bromotoluene yielded about 24 per cent of o-bromobenzoic acid, and o-chlorotoluene about 14 per cent of o-chlorobenzoic acid. o-Nitrotoluene, however, decomposed to such an extent that very little or practically none of the corresponding acid could be obtained.

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[102] *Trans. Amer. Electrochem. Soc.*, 1929, 56, 495; *Brit. Chem. Abs.* **B**, 1929, 972.

[103] Fichter and Rinderspacher, *Helv. Chim. Acta*, 1926, 9, 1097; *Brit. Chem. Abs.* **A**, 1927, 48.

[104] *Trans. Amer. Electrochem. Soc.*, 1929, 56, 477; *Brit. Chem. Abs.* **B**, 1929, 886.

[105] British Patent 265,672, 1925; *Chem. Abs.*, 1928, 22, 359.

[106] Maxted and Dunsby, *J.C.S.*, 1928, 1439.

Acenaphthene vapors when mixed with 9 to 12 volumes of air and passed over manganese dioxide or an oxide of vanadium or molybdenum at about 400° C. yielded a mixture of acenaphthylene, acenaphthenequinone, and naphthalic anhydride. The products could be separated by fractional condensation.[107] Among the catalysts employed by Jaeger[107a] for the vapor-phase oxidation of acenaphthene are compounds of alkali and alkaline earth metals, molybdenum, tungsten, uranium, chromium, iron, silver, manganese, aluminum, nickel, and cobalt.

β-Naphthol heated to 300° C. in contact with air in the presence of either tungsten or molybdenum trioxides gave 2,2′-dinaphthyl ether.[108] Under similar conditions but employing vanadium pentoxide, *β*-dinaphthol was obtained. At 340° C., 1,1′-dinaphthylene-2,2′-oxide was formed, though in the absence of air only the 2,2′-dinaphthyl ether was produced. When titanium dioxide was used, the product was mainly 2,2′-dinaphthyl ether together with some 1,1′-dinaphthylene-2,2′-oxide.

Lucas and Bibb[109] have shown that a mixture of benzene vapor and air, containing a small quantity of nitric acid vapor or oxides of nitrogen as catalysts, passed through a tube at 600° to 750° C. yields some phenol. By regulating the conditions, such as rate of flow, concentration of the catalyst, and temperature of the tube, 5 to 5.5 per cent of the benzene was oxidized to phenol.

Benzoic acid and p-nitrobenzoic acid are the main products if toluene is boiled with nitric acid.[110] Some o-nitrotoluene, carbon dioxide and traces of picric acid are also formed. No p-nitrotoluene was obtained as this substance is comparatively easily oxidized to p-nitrobenzoic acid. Little difference was noticed in the results obtained by oxidizing under 10 and 15 atmospheres pressure.[111] Reaction proceeds slowly at 150° C., much faster at 180° to 185° C., and above 190° C. there is a tendency to explode. Benzoic acid was recovered almost quantitatively when toluene was heated with 22.5 per cent nitric acid at 180° to 185° C. under 10 to 20 atmospheres of oxygen.

Oxidation of hydroaromatic compounds can be effected with nitric acid. Cyclohexanol, for example, may be oxidized with 50 per cent nitric acid at 50° C. in the presence of a small quantity of ammonium vanadate.[112] This operation yields principally adipic acid, together with small proportions of both glutaric and succinic acids. The vapor phase oxidation of methylcyclohexanol with air at 300° to 400° C., using vanadic acid as a catalyst, also gives adipic acid.[113] A mixture of cis- and trans-hexahydro-o-phenylenediacetic acid, with some octahydrocinnamic-o-carboxylic acid, results from the treatment of decahydronaphthol with 60 per cent nitric acid at 50° C. in the presence of ammonium vanadate.[114]

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[107] Lewis, U. S. Patent 1,649,833, Nov. 22, 1927; assigned to National Aniline and Chemical Co.; *Brit. Chem. Abs.* **B**, 1928, 152.

[107a] U. S. Patents 1,844,390 and 1,844,392, Feb. 9, 1932; *Chem. Abs.*, 1932, **26**, 1947; British Patent 318,617, 1928; *Chem. Abs.*, 1930, **24**, 2145; Jaeger and Norton, U. S. Patent 1,844,391, Feb. 9, 1932; *Chem. Abs.*, 1932, **26**, 1947; all patents assigned to Selden Co.

[108] Clemo and Spence, *J.C.S.*, 1928, 2811.

[109] *Ind. Eng. Chem.*, 1929, **21**, 635.

[110] Askenasy, Elöd and Trogus, *Ann.*, 1928, **461**, 109; *Brit. Chem. Abs.* **A**, 1928, 746.

[111] See also Chemische Fabriken Worms A.-G., French Patent 529,461, 1921.

[112] Riedel, British Patent 265,959, 1927; *Brit. Chem. Abs.* **B**, 1928, 117. *Cf.* Schrauth, U. S. Patent 1,921,101, Aug. 8, 1933; assigned to E. I. duPont de Nemours & Co., Inc.; *Chem. Abs.*, 1933, **27**, 5084.

[113] Deutsche Hydrierwerke A.-G., German Patent 473,960, 1926; *Chem. Abs.*, 1929, **23**, 2988. The action of free oxygen on hydroaromatic compounds has been discussed by Chavanne, Miller and Cornet (*Bull. soc. chim. Belg.*, 1931, **40**, 673; *Brit. Chem. Abs.* **A**, 1932, 372) and by Wienhaus (*Z. angew. Chem.*, 1928, **41**, 617).

Binapfl[114a] treated tetrahydronaphthalene at 100° C. for 9 hours with air or oxygen in the presence of nitrocellulose and benzyl nitrate, the products being α-ketotetrahydronaphthalene and α-hydroxytetrahydronaphthalene. The oxidation of side chains of aromatic compounds such as methylbenzanthrone has been effected by heating them with selenious or selenic acid.[114b] The aromatic ring is said to be unattacked by this treatment and the oxidation proceeds to the formation of aldehyde, carboxyl or ketonic groups.

Benzene and its homologues absorb ozone like unsaturated compounds.[115] This absorption, however, is not complete, even though ozone is present in large excess.[116] Compounds such as styrene and phenylcyclohexene add ozone at the ethylenic linkage and when this addition is complete the nucleus is attacked. Acetylenic hydrocarbons, in their behavior towards ozone, are intermediate between ethylenic and benzenoid hydrocarbons. Ozonization curves can be used to distinguish sharply between these three types of hydrocarbons.

Instead of air or oxygen, carbon dioxide can be employed in some instances as an oxidizing agent. For example, toluene and anthracene are oxidized to benzaldehyde and anthraquinone, respectively, by conducting the vapors of these compounds mixed with moist carbon dioxide over vanadic acid deposited on pumice at 480° to 500° C.[117]

The treatment of coal with potassium permanganate at 70° to 130° C. to yield aromatic carboxylic acids, of which mellitic acid is the chief constituent, has been described by Bone and Quarendon.[117a]

Kinney and Langlois[117b] observed that, with catalysts of the zinc-copper-chromium oxide type, benzene was directly carboxylated to benzoic acid at about 300° C. under a pressure of 30 atmospheres. The yield of acid was low, however, but was increased in a further study by Kinney and Ward[117c] by the use of a similar catalyst prepared in a different manner. In this later investigation, diphenylmethane, triphenylmethane, styrene, phenol, anisol (phenyl ethyl ether) bromobenzene, dimethylaniline, nitrobenzene, catechol, resorcinol and quinol, but not phenol, were also carboxylated by this treatment. Similar treatment of diisopropylbenzene or cuminol with carbon dioxide in the presence of aluminum chloride, cuprous chloride or hydrogen chloride has been said to yield diisopropylbenzaldehyde.[117d]

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[114] Deutsche Hydrierwerke A.-G., German Patent 474,985, 1926; *Chem. Abs.*, 1929, **23**, 2988.

[114a] German Patent 537,434, 1929; *Chem. Abs.*, 1932, **26**, 1296; German Patent 539,476, 1929; *Chem. Abs.*, 1932, **26**, 1614; both patents assigned to I. G. Farbenindustrie A.-G.

[114b] I. G. Farbenindustrie A.-G., British Patent 347,743, 1930; *Chem. Abs.*, 1932, **26**, 2748.

[115] Harries and Weiss, *Ber.*, 1904, **37**, 3431. Houzeau and Renard. *Compt. rend.*, 1873, **76**, 572; Renard, *ibid.*, 1895, **120**, 1177. Leeds, *Ber.*, 1881, **14**, 975.

[116] Brus and Peyresblanques, *Compt. rend.*, 1930, **190**, 685; *Brit. Chem. Abs.* **A**, 1930, 588.

[117] Schmidt, Seydel and Ufer, German Patent 408,184, 1920; assigned to Badische Anilin- und Soda-Fabrik; *J.S.C.I.*, 1925, **44**, 475B.

[117a] British Patent 286,006, 1925; assigned to Gas Light and Coke Co.; *Brit. Chem. Abs.* **B**, 1927, 402.

[117b] *J.A.C.S.*, 1931, **53**, 2189.

[117c] *J.A.C.S.*, 1933, **55**, 3796.

[117d] I. G. Farbenindustrie A.-G., British Patent 293,703, 1927; *Chem. Abs.*, 1929, **23**, 1649.

Chapter 42

Production of Acids from Petroleum Hydrocarbons

Methods of producing acids from hydrocarbons by oxidation may be classified roughly into three main divisions:

(1) The oxidation of hydrocarbons by air, oxygen, nitrogen dioxide, or other gaseous oxidizing agents. This type of reaction may be accelerated by catalysts, and the hydrocarbons can be gases, liquids or solids. This method appears to be most promising from an industrial point of view.

(2) The oxidation of hydrocarbons by ozone. The low yields generally obtained by this method appear to limit its application materially.

(3) The conversion of halogen derivatives of the hydrocarbons, particularly chlorides, to unsaturated compounds and subsequently to acids by oxidation. This method is perhaps too complicated for any extensive industrial adaptation.

In this chapter the production of acids from both gaseous and liquid hydrocarbons by vapor and liquid phase oxidation is discussed. Some oxidation processes which yield acids and a variety of other products have also been mentioned in a preceding chapter (36). The oxidation of solid hydrocarbons (such as paraffin wax) is described in the next chapter. The acids obtained from heavy petroleum distillates resemble, more or less, the "wax acids" produced from paraffin wax.[1]

OXIDATION OF GASEOUS HYDROCARBONS

Methane can be oxidized to formaldehyde, as described in Chapter 38, and formaldehyde to formic acid. Numerous attempts have been made to produce formic acid by reaction between carbon monoxide and water, thus:

$$(1)\quad CH_4 + O_2 \longrightarrow CO + H_2O + H_2$$

$$(2)\quad CO + H_2O \longrightarrow HCOOH$$

Reaction (1) is, of course, that involved in the partial oxidation of methane to produce hydrogen from natural gas.[2] Reaction (2), however, is a reaction not particularly pertinent to this chapter. Syntheses with carbon monoxide[3] are too far removed from the scope of this volume, hence only a few which pertain to the production of formic acid are given.

Nielsen[4] proposed to effect the partial oxidation of methane to formic acid in the presence of a copper suboxide catalyst at temperatures which are said to range from 250° to 800° C. The process is not continuous since the catalyst becomes reduced and requires reoxidation.

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[1] Danaila and Boltus-Goruneanu (*Bul. chim. soc. romana stiinte,* 1929, 31, 133-200; *Chem. Abs.*, 1930, 24, 2282; *Chem. Zentr.,* 1931, 1, 1393) believed that only the acids from paraffin wax can have practical application—those from mineral oils being semi-solid acids resembling humic acids, of objectionable odor and color, which they state are useless in the manufacture of soap. These investigators reviewed the literature from 1855.

[2] This reaction is discussed more completely in Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 1930, 771; see also Chapter 8 of this book; Marek and Hahn, "Catalytic Oxidation of Organic Compounds in the Vapor Phase," Chemical Catalog Co., Inc., New York, 1932, 259.

[3] For detailed information on this subject see Ellis, *op. cit.*, 652, *et seq.*

[4] U. S. Patent 1,665,175, Apr. 3, 1928; *Chem. Abs.*, 1928, 22, 1832. See also Nielsen, U. S. Patent 1,672,081, June 5, 1928; British Patent 198,385, 1921; *J.S.C.I.*, 1923, 42, 760A.

Dreyfus[5] stated that when methane together with carbon monoxide or carbon dioxide is passed under pressure over heated catalysts, a mixture of acetic acid, acetaldehyde, and acetone is formed. The temperature during the reaction can range between 120° and 350° C., and the pressure from 12 to 500 atmospheres. The catalysts may be (1) copper, iron, nickel, cobalt, platinum, palladium, platinum or palladium black, ferrites, ferrates, cobaltites or cobaltates of alkali or alkaline earth metals used in conjunction with zinc, magnesium, calcium, aluminum, chromium, molybdenum and vanadium or (2) carbonates which dissociate below 500° C., as for example nickel carbonate.

The reactions involved in this process have been known for a long time.[6] Moldavski,[7] by thermodynamic calculations[8] and by experiment, showed that this procedure is not feasible economically. In his tests, Moldavski obtained an acetic acid yield of 0.00001 per cent on passing the gases once over a catalyst made by heating nickel formate to 200° to 250° C.[9]

Acetaldehyde, which is one of the partial oxidation products of gaseous hydrocarbons (see Chapter 38), can be further oxidized to acetic acid by passing its vapors together with air over copper or platinum at 150° to 200° C.[10] The oxidation of acetaldehyde or its solutions can also be effected by conducting the vapors countercurrent to a stream of air through a series of towers maintained at gradually increasing temperatures.[11]

In a study of the oxidation of acetaldehyde with oxygen, Pease[12] came to the following conclusions: (1) Peracetic acid is the largest product except when the reaction vessel is coated with potassium chloride; (2) the reaction is accelerated by broken glass packing, and by coating the vessel with potassium chloride; (3) the reaction is inhibited by ethyl alcohol vapor but not by water vapor. Nitrogen, hydrogen and ethane are without effect on the rate. (4) The initial rate is proportional to the square of the acetaldehyde concentration and independent of the oxygen concentration. (5) The reaction is auto-accelerated and is believed to be of the chain type, with chains starting on the walls and ending in the gas phase.

Butyraldehyde may also be oxidized by oxygen producing butyric acid.[13]

The indirect oxidation of ethylene to acetic acid can be effected by converting it to ethyl alcohol (see Chapter 13) which can then be oxidized to acetic acid either (1) electrolytically, (2) with chromic acid or potassium permanganate, or (3) by air.[14] Strache[15] described a method in which unsaturated hydrocarbons, obtained from a variety of sources, are esterified with a mineral acid, such as sulphuric acid, and then oxidized with potassium dichromate. Volatile acids can be separated from the products by steam-distillation.

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[5] British Patent 226,248, 1923; *Chem. Abs.*, 1925, **19**, 2057. See also French Patent 581,908, 1924; French Patent 737,610, 1932; *Chem. Abs.*, 1933, **27**, 1642; *Quim. e ind.*, 1930, 305; Mullin and Hunter, *Chemical Markets*, 1931, **29**, 380, 482; *Chem. Abs.*, 1932, **26**, 1897; Dreyfus and Bader, U. S. Patents 1,864,531 and 1,864,643, June 28, 1932; assigned to Celanese Corp. of America; *Chem. Abs.*, 1932, **26**, 4346.

[6] See Pasquin, *Metallbörse*, 1932, **22**, 563; *Chem. Abs.*, 1932, **26**, 3879; Dreyfus, British Patent 337,014, 1929; *Brit. Chem. Abs.* **B**, 1931, 148; British Patent 337,410, 1929; *Brit. Chem. Abs.* **B**, 1931, 194.

[7] *J. Appl. Chem. (U.S.S.R.)*, 1931, **4**, 667; *Chem. Abs.*, 1932, **26**, 964.

[8] The possibility of synthesizing carboxylic acids from aromatic hydrocarbons and carbon dioxide has also been shown to be thermodynamically impossible by Parks and Huffman, and by Bonner (personal communication).

[9] *Cf.* Pasquin, *loc. cit.*

[10] Dreyfus, British Patents 105,065, 1917; *Chem. Abs.*, 1917, **11**, 2137; British Patent 108,459, 1918; *Chem. Abs.*, 1917, **11**, 3041; British Patent 110,545, 1919; *Chem. Abs.*, 1918, **12**, 484. See Marek and Hahn, *op. cit.*, 97.

[11] Young and Herrly, U. S. Patent 1,620,180, Mar. 8, 1927; assigned to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1927, 378.

[12] *J.A.C.S.*, 1933, **55**, 2753.

[13] Young, Canadian Patent 245,157, 1924; *Chem. Abs.*, 1925, **19**, 657.

[14] See Usher and Venkateswaran, *J.S.C.I.*, 1918, **37**, 194R.

[15] British Patent 147,905, 1920; *Chem. Abs.*, 1921, **15**, 168; German Patent 344,877, 1917; *J.S.C.I.*, 1922, **41**, 210A.

Acetic acid may be produced from acetylene[16] by passing this gas together with hydrogen and air, the latter being added in stages, over the vanadates of tin, silver, or mercury at 200° to 250° C.

OXIDATION OF LIQUID HYDROCARBONS IN THE LIQUID PHASE

One of the earliest investigators of the production of organic acids from petroleum hydrocarbons was Schaal.[17] His work included the oxidation of not only petroleum hydrocarbons but also those resulting from the distillation of coal, shale and peat. In the oxidation air was passed into a mixture of hydrocarbons and alkalies, such as the carbonates or hydroxides of the alkali or alkaline earth metals, heated under pressure. Additional alkali was added from time to time during the heating so as to maintain always a slight excess. Copper was found to be a good catalyst. Pumice, infusorial earth, sodium chloride and sulphate also aided the reaction. After the oxidation, the soluble materials were removed with as little water as possible, leaving the acids dissolved in the petroleum. These acids were then extracted with alkalies and afterwards liberated by the addition of mineral acids.[18]

In several instances the hydrocarbons were difficult to oxidize, in which event oxidation was started by the use of bleaching powder. With this reagent the hydrocarbon mixture had to be cooled frequently to avoid too violent a reaction. At the end of the oxidation the lime was removed with hydrochloric acid and the organic acids were extracted from the oil with alkalies. The residual oil could then be oxidized further with air.

Löffl[19] oxidized petroleum fractions at 115° to 120° C. under 3 atmospheres pressure in the presence of water.[20] Lead and mercury compounds were recommended as catalysts. The products were acids together with some aldehydes and ketones, which were fractionated by distillation up to 200° C. with superheated steam and then by steam distillation *in vacuo.*

Zerner[21] produced acids by the oxidation of liquid hydrocarbons obtained on the distillation of petroleum in the following manner: the hydrocarbon was treated with liquid sulphur dioxide, to remove unsaturated compounds, and then blown with air or other oxygen-containing gases, in the presence of bases. Fuming sulphuric acid can be used in place of liquid sulphur dioxide to remove constituents which form resinous or asphaltic substances. This preliminary refining, however, may be eliminated in one of two ways: (1) the reaction-promoting agents which are formed by blowing the liquid hydrocarbons in an acid medium are added to the hydrocarbons before treating in the presence of a base, or (2) the liquid hydrocarbons may be blown first in the presence of an acid and the treatment afterwards continued in the presence of a base.[22] The refining may be eliminated entirely if oxidation is carried out in steps in the presence of a base and detrimental reaction products are removed between steps by filtration.[23] Luther and Harder [23a] suggested a preliminary purification of paraffin or naphthene hydrocarbons by treating with dilute nitric acid at 80° to 100° C., and subsequently with concentrated sulphuric acid. Pressure hydrogenation in the presence of metals of groups IV to VII have been proposed for the removal of sulphur compounds prior to oxidation of hydrocarbons by air with a manganese stearate catalyst.[23b]

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[16] I. G. Farbenindustrie A.-G., British Patent 304,855, 1927; *Brit. Chem. Abs.* **B**, 1929, 315.

[17] British Patent 12,806, 1884; *J.S.C.I.*, 1885, **4**, 679; U. S. Patent 335,962, Feb. 9, 1886; German Patent 32,705, 1884.

[18] For a method of acid separation by alkali treatment see Standard Oil Development Co., French Patent 658,417, 1928; *Chem. Abs.*, 1929, **23**, 5195.

[19] *Chem. Ztg.*, 1920, **44**, 561; *J.S.C.I.*, 1920, **39**, 604A.

[20] Water was also observed to increase the oxidizability of Caucasian petroleums. (Ivanov and Petin, *J. Gen. Chem. Russia,* 1931, **1**, 704; *Brit. Chem. Abs.* **B**, 1932, 409).

[21] British Patent 174,611, 1921; *Chem. Abs.*, 1922, **16**, 1878. U. S. Patent 1,436,136, Nov. 21, 1923; *Chem. Abs.*, 1923, **17**, 63.

[22] Winternitz, Bullinger and Teichner, British Patent 174,642, 1922; *Chem. Abs.*, 1922, **16**, 1878.

Oxidation of Caucasian oil at 140° C. by air in the presence of fuming sulphuric acid yielded about 5 per cent crude acids.[24] Of the crude acids approximately 60 per cent was soluble in benzene and the remainder, acids and resins, was insoluble.[25]

The work of Tuichinin and Ivanov [26] indicated that treatment with liquid sulphur dioxide or with 50 per cent alcohol increased the oxidizability of a Baku gas oil more than did anhydrous sulphuric acid. Poor results were obtained with oleum, however.

In comparing the catalytic action of various metals, Petrov, Danilovich and Rabinovich [27] oxidized petrolatum oil at 100° to 105° C. in the presence of powdered lead, iron and zinc. Of these metals, lead proved to be the best, yielding about 2.6 to 3.6 per cent acids. With the other metals the yields were less or no more acids (0.41 to 0.7 per cent) than were produced in the absence of the catalyst. The oil, however, after being refined with sulphuric acid and alkali, was not oxidized when exposed to a current of air for 49 hours at 100° C., either in the presence or absence of zinc or iron. Lead catalyzed the formation of hydroxy-acids which were insoluble in benzene.

Arditti [28] observed that with zinc and lead, oxidation of paraffin oil at 130° C. is faster at first but after some time it becomes even slower than in the absence of a metallic catalyst. Copper and nickel definitely hasten the reaction but sulphur retards it.

In the oxidation of paraffin oils, Tütünnikoff [29] used manganic oxide, manganese dioxide, and red lead oxide as catalysts. The lead oxide was found to be the best catalyst. By long passage of air it was possible to oxidize 90 per cent of the oil. The paraffin oil yielded chiefly saturated acids.

Metallic salts of organic acids are also used as oxidation catalysts. For example, Teichner [30] oxidized Galician spindle oil which had been freed of unsaturated compounds by treatment with 20 per cent oleum, with air or oxygen at 110° C. in the presence of zinc stearate.

Liquid petroleum hydrocarbons are oxidized under a pressure of 100 to 320 pounds per square inch, at temperatures of about 120° to 130° C., with manganese stearate or oleate as a catalyst, in a method developed by Burwell.[31] If oxidation is carried on until about 20 per cent of the hydrocarbons are oxidized, the products are principally the simple carboxylic acids. Hydroxy-acids predominate when the oxidation is conducted to the extent of about 80 per cent. The type of distillate being oxidized also determines to some extent the kind of acid which will be present in the larger proportion. The two types of acids may be separated[32] in several ways: In one method, fresh oil is added to the oxidized mixture. The simple carboxylic acids are thus dissolved and the hydroxy-acids can then be withdrawn. The mixed acids can also be separated with concentrated sulphuric acid, which dissolves the hydroxy-acids but not the simple carboxylic acids.[33] It is also possible to partially oxidize the hydrocarbons, withdraw the products insoluble in the hydrocarbon mixture, and then continue oxidation. The products obtained by the oxidation of a 42° Bé distillate from Pennsylvania crude oil by Burwell's procedure were: 5 per cent formic acid, 5 per cent of acids varying from $C_7H_{14}O_2$ to $C_{12}H_{24}O_2$, and 90 to 95 per cent of liquid acids having an average molecular weight greater than 345.

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[23] Winternitz, Bullinger and Teichner, British Patent 174,643, 1922; *Chem. Abs.*, 1922, **16**, 1878.

[23a] German Patent 566,449, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 991.

[23b] I. G. Farbenindustrie A.-G., British Patent 363,711, 1930; *Brit. Chem. Abs.* **B**, 1932, 249.

[24] Petrov and Danilovich, *Trans. Karpov. Inst. Chem.* (*Russia*), 1925, **4**, 143; *Chem.-Abs.*, 1926, **20**, 1512.

[25] Resinous substances, as pointed out by Tschernoshukov (*Isvestia Thermo-Tech. Inst., Moscow*, 1928, **6**, 7; *Brit. Chem. Abs.* **B**, 1929, 85) may result from acids by loss of carbon dioxide and subsequent condensation of the unsaturated hydrocarbons thus formed and also by condensations of aldehydes.

[26] *Neft. Khoz.*, 1930, **18**, 979; *Brit. Chem. Abs.* **B**, 1931, 284.

[27] *Seifensieder-Ztg.*, 1926, **53**, 475, 494; *Chem. Abs.*, 1926, **20**, 3074. Also *Trans. Karpov. Inst. Chem.*, 1926, No. 5, 81; *Chem. Abs.*, 1928, **22**, 2073.

[28] *Compt. rend.*, 1931, **193**, 589; *Chem. Abs.*, 1932, **26**, 1234.

[29] *Z. angew. Chem.*, 1924, **37**, 300; *Chem. Abs.*, 1924, **18**, 2423.

[30] British Patent 148,358, 1920; Canadian Patent 218,215, 1922; U. S. Patent 1,436,214, Nov. 21, 1922; *Chem. Abs.*, 1923, **17**, 631.

[31] U. S. Patents 1,690,768 and 1,690,769, Nov. 6, 1928; *Chem. Abs.*, 1929, **23**, 509. U. S. Patent 1,828,356, Oct. 20, 1931; *Chem. Abs.*, 1932, **26**, 737. British Patents 309,382, 309,383, and

Dietrich[34] destroyed hydroxy acids by heating the oxidation products of high molecular hydrocarbons in the presence of catalysts which have a dehydrating effect. For instance, the crude product obtained from the oxidation of gas oil was heated for 4 hours at 250° C. and under 50 atmospheres pressure in the presence of naphthalenemonosulphonic acid, nickel and hydrogen. The solubility of the initial substance in petroleum ether changed from 58.2 to 91.8 per cent, and the iodine value from 17.8 to 46.7.

In addition to the metallic salts of fatty acids, Petrov and his collaborators[35] showed that metallic salts of naphthenic acids also can be used for the oxidation of oils. With an acid-treated Caucasian oil the yield of acids on oxidation was considerably increased by the presence of cobalt naphthenate. This same substance also produced a much higher yield of acids than did lead, which had proven to be the best metallic catalyst.[36] The activities of various naphthenates were compared by these same investigators. Manganese naphthenates were the most and zinc naphthenates the least active. Copper and lead naphthenates were intermediate in activity.[37] The manganese salts of sulpho-acids of high molecular weight were the most active catalysts. It was observed that oils refined with sulphuric acid were oxidized to about the same extent as unrefined oils. The former, however, yielded the larger quantity of soluble acids and the latter gave more hydroxy-acids. Distilled oils which were highly refined with sulphuric acid were not oxidized in the absence of a catalyst but darkened as a result of decomposition. The oxidizability of an acid-treated oil, however, can be increased also by the addition of the lithium, sodium, potassium, or iron salts of naphthenic acids.[38]

309,384, 1927; *Chem. Abs.*, 1930, **24**, 717; see also U. S. Patent 1,770,875, July 15, 1930; *Chem. Abs.*, 1930, **24**, 4647; U. S. Patent 1,895,374, Jan. 24, 1933; *Chem. Abs.*, 1933, **27**, 2572; all patents assigned to Alox Chemical Co.

[32] Stetzenko and Buman (*Masloboino-Zhirovoe Delo,* 1932, No. 9, 18; *Chem. Abs.*, 1933, **27**, 3354) found that the detergency of hydroxy-acids which form in the oxidation of solar oils is about equal to that of the carboxylic acids, hence, this separation may not be necessary in many cases in which the acids are to be used in soap manufacture. The acids had about one-half to one-third the detergent power of fatty acid soaps and were similar in properties to the soaps of naphthenic acids. See also Hellthaler and Peter, German Patent 546,913, 1933; *Chem. Abs.*, 1933, **27**, 4249; Dovankov, *Masloboino-Zhirovoe Delo,* 1932, No. 1, 54; *Brit. Chem. Abs.* **B**, 1933, **27**, 661.

[33] *Cf.* Dovankov, *Masloboino-Zhirovoe Delo,* 1932, No. 1, 54; *Chem. Abs.*, 1932, **26**, 4704; *ibid.*, 1933, **27**, 2424.

[34] German Patent 575,950, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4813.

[35] Petrov, Danilovich and Rabinovich, *Trans. Karpov. Inst. Chem.* (*Russia*), 1925, **4**, 143; *Chem. Abs.*, 1926, **20**, 1512. *Trans. Karpov. Inst. Chem.* (*Russia*), 1926, **5**, 81; *Chem. Abs.*, 1928, **22**, 2073.

[36] Petrov, Danilovich and Rabinovich, *Seifensieder-Ztg.*, 1926, **53**, 475, 494; *Chem. Abs.*, 1926, **20**, 3074.

[37] Petrov, Danilovich and Rabinovich, *Papers Karpov. Chem. Inst., Bach Mem. Vol.*, 1927, **157**; *Brit. Chem. Abs.* **B**, 1929, 7.

[38] Tuichinin and Ivanov, *Neft. Khoz.*, 1930, **18**, 979; *Brit. Chem. Abs.* **B**, 1931, 284.

Dietrich and Harder[38a] obtained high-molecular oxygenated compounds by oxidizing Pennsylvania middle oil with a five-stage air treatment at 160° C. in the presence of manganese naphthenate. The mixture obtained was first treated with sodium hydroxide to remove the acids formed and then the residue hydrogenated at 200° C. with a nickel-kieselguhr catalyst. On shaking the resulting mixture with liquid sulphur dioxide, two layers formed, the upper containing hydrocarbons of hydroxyl number 1.3, and the lower, alcohols of hydroxyl number 95.

In oxidizing mineral oils to acids, Zerner[39] used, among other catalysts, manganese resinate and turpentine. Only catalysts containing a metal, especially manganese, were found to start the oxidation at low temperatures, and variations in the quantities of catalyst used, from 0.1 to 5 per cent, made little difference. He considered the disagreeable odor of the products to be a disadvantage in their use for soap making.

As catalysts for the oxidation of mineral oils to acids, acetylacetonates of manganese, cerium, nickel, cobalt, or zinc have also been suggested.[40] Metallic oxides may be added at the same time.

Luther and Klein[40a] suggested the use of aliphatic saturated carboxylic acids containing up to four carbon atoms in the molecule. They subjected the hydrocarbons in the liquid phase, to which had been added from 2 to 20 per cent of formic, acetic, or propionic acid, to treatment with oxidizing gases at 80° to 200° C. under pressures as high as 50 atmospheres. Resinates or oleates of alkali or alkaline-earth metals, aluminum, magnesium or manganese, and solid bodies of aluminum, or inert bodies such as glass and porcelain, may be employed as catalysts. Explosions are prevented by controlling the ratio of oxidizing gas to the hydrocarbon liquid by dilution with an inert gas, such as carbon dioxide. In this method esters are formed by the reaction of the resulting alcohols and the added acids. The esters are not attacked by the oxidizing agents and no resinification or polymerization takes place.

Activated carbon, obtained from vegetable raw material in such a manner that the structure of the raw material is retained, has also been proposed as a catalyst for the oxidation of oils.[41] The carbonized material may be used in one of three ways: (1) It is mixed with the liquid and the mixture under pressure is treated with the oxidizing gas. (2) The liquid and gas can be passed, countercurrently, through a column filled with the granular carbon. Or, (3) the carbon can be made to adsorb the oxidizing gas, for example, at low temperatures under pressure, and the liquid is then treated with the charged carbon.

Yamada[42] studied the effect of oxidation at 130° C. on the acid saponification and acetyl values of a petrolatum and a switch oil. These values increase almost linearly with the time, but the acetyl value of the unsaponifiable fraction shows a definite maximum.

[38a] German Patent 559,522, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 730.

[39] *Chem. Age*, 1930, **23**, 254. See also Flammer and Kelber, German Patent 406,866, 1919; *J.S.C.I.*, 1925, **44**, 338B.

[40] Luther and Klein, U. S. Patent 1,872,774, Aug. 23, 1932; *Chem. Abs.*, 1932, **26**, 5963; British Patent 303,268, 1927; *Chem. Abs.*, 1929, **23**, 4567; both patents assigned to I. G. Farbenindustrie A.-G.

[40a] U. S. Patent 1,864,079, June 21, 1932; *Chem. Abs.*, 1932, **26**, 4343; *cf.* British Patent 345,391, 1930; *Brit. Chem. Abs.* **B**, 1931, 666; addition to British Patent 312,388, 1928; *Brit. Chem. Abs.* **B**, 1929, 746; German Patent 570,732, 1933; *Chem. Abs.*, 1933, **27**, 4238; German Patent 539,572, 1928; *Chem. Abs.*, 1932, **26**, 2194; all patents assigned to I. G. Farbenindustrie A.-G.; Dietrich and Luther, German Patent 581,238, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 5082. I. G. Farbenindustrie A.-G. (British Patent 353.047, 1930; *Brit. Chem. Abs.* **B**, 1931, 1132) applies this same method in treating hydrocarbons with boiling point above 180° C. (see Chapter 43).

[41] Algemeene Norit Maatschappij, British Patent 188,667, 1923; *Chem. Abs.*, 1923, **17**, 1678.

[42] *J. Soc. Chem. Ind. Japan*, 1931, **34**, 188B; *Brit. Chem. Abs.* **B**, 1931, 829.

OXIDATION OF LIQUID HYDROCARBONS IN THE VAPOR PHASE

The vapor-phase oxidation of light distillates has been discussed in Chapter 36. Examples are described by Ellis,[43] in which a petroleum distillate is cracked by being passed through a heated zone and the vapors are mixed with air, or oxygen, and conducted over a heated catalyst. Both mono- and di-basic acids, such as formic, acetic, maleic and phthalic, are obtained. Shimose[44] also showed that vapor-phase catalytic oxidation of both saturated and unsaturated hydrocarbons leads to the production principally of maleic acid, together with carbon dioxide and formaldehyde.

Schill and Seilacher[45] dispersed heated grease or oil in the form of a spray with a hot blast of air. Part of the spray condenses immediately, but the greater portion is passed through a series of chambers, allowing longer contact for oxidation. Ozonized air or a mixture of ammonia and air can be used. The products may be employed in the manufacture of leather and soap, and in dyeing as a substitute for tournante oil.

In a process developed by Walter[46] the petroleum distillate, boiling above 300° C., is sprayed into a current of air mixed with steam. After being conducted over a catalyst, consisting of asbestos coated with finely divided copper oxide, which is kept at a red heat, the mixture is cooled in a condensing apparatus. By regulating the proportions of air and steam it is possible to keep the catalyst at a red heat without the application of heat from an outside source. The aqueous layer of condensed products contains acetic acid and its homologues. From the oily top layer it is possible to extract the water-insoluble acids with alkaline solutions. Aldehydes can be separated from the organic acids with sodium bisulphite.

This method of oxidizing liquid petroleum distillates has been modified as follows:[47] The liquid is sprayed through atomizers into the top of a tower which is kept at 80° C. and is packed with pumice impregnated with nickel oxide. At the bottom of the tower either oxygen or oxygen diluted with nitrogen is introduced. The gases leave the tower at the upper end and, after passing through condensers and scrubbers, can be used over again with the addition of fresh oxygen. The hydrocarbons pass out of the lower end of the tower into reservoirs, and from there through the apparatus again until sufficient oxidation has been effected. This method of oxidation favors the production of high molecular weight, water-insoluble acids. Blowing of the distillate results in the formation of considerable quantities of alcohols, esters, and low molecular weight, water-soluble acids.

To oxidize low-boiling aliphatic hydrocarbons to acids Wiezevich and Tannich[48] circulated the gases together with air through a non-catalytic partial oxidation zone under pressures[49] of 300 to 3000 pounds per square inch at temperatures of 200° to 600° C.

Aldehyde-acids have been found to form as the principal products when liquid hydrocarbons are oxidized at high temperatures. To produce aldehydes and aldehyde-acids,[50] the vapors of the liquid hydrocarbons together with air, or other oxygen-containing gas, are passed over metallic oxides at 500° C. Oxides of molybdenum, especially the "blue oxide," appear to be the best catalysts. The quantity of oxygen actually present in the gas is generally slightly in excess of that required stoichiometrically, and steam can be added to lessen the risk of explosion. The condensed products contained, as a typical example, about 70 per cent aldehyde-acids, 25 per cent aldehydes, and about 5 per cent unchanged hydrocarbons together with undetermined substances.

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[43] U. S. Patent 1,516,720, Nov. 25, 1924; U. S. Patents 1,697,262, 1,697,263, 1,697,264, 1,697,265, 1,697,266, and 1,697,267, Jan. 1, 1929; assigned to Ellis-Foster Co.

[44] *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1931, **15**, 251; *Chem. Abs.*, 1931, **25**, 4694.

[45] British Patent 12,799, 1886; *J.S.C.I.*, 1887, **6**, 549.

[46] British Patent 21,941, 1905; *J.S.C.I.*, 1906, **25**, 1173. French Patent 360,785, 1905; *J.S.C.I.*, 1906, **25**, 493. German Patent 168,291, 1904; *Chem. Zentr.*, 1906, 1, 1199.

[47] Deutsche Erdöl A.-G., British Patent 148,892, 1920; *J.S.C.I.*, 1921, **40**, 729A.

[48] U. S. Patent 1,838,032, Dec. 22, 1931; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1932, **26**, 1300.

[49] Pressure is also recommended by Soc. française de catalyse généralisée, French Patent 726,074, 1931; *Chem. Abs.*, 1932, **26**, 4973.

The aldehyde-acids can be separated from the other materials by precipitation as insoluble salts, such as those of aluminum.[51] The solution of the aldehydes and aldehyde-acids is agitated with the hydroxide of the metal and the insoluble salt thus formed is removed by filtration or decantation. Or the mixture containing aldehyde, aldehyde-acids, and hydrocarbons can be heated to 100° C. with the carbonate or hydroxide of the metal. On cooling, the soap separates from this mass and can be easily removed. Numerous derivatives of these oxidized products have been proposed.[52]

Efforts have been made to eliminate the disagreeable odor associated with the soaps of the aldehyde-acids by converting these acids to dibasic acids.[53] The oxidation can be carried out with nitric acid or with nitrogen dioxide in the presence of vanadium pentoxide or molybdenum trioxide or the acids, dissolved in water, may be oxidized with chlorine in the presence of cobalt chloride. The soaps themselves can also be oxidized with chlorine provided the medium is kept alkaline. In some instances the aldehyde-acids can be oxidized to dibasic acids in the vapor phase with air or oxygen in the presence of a uranyl molybdate catalyst.

OXIDATION OF LIQUID HYDROCARBONS BY OTHER OXIDIZING AGENTS

Acids, as well as esters, are obtained when petroleum benzines which boil below 180° C. are oxidized at temperatures varying from 80° to 200° C., under 50 atmospheres pressure, with oxides of nitrogen.[54] Resinates, oleates, and enolates of the alkali and alkaline earth metals, magnesium, aluminum or manganese can be used as catalysts. The products from the oxidation of hexane, for example, under these conditions contained the lower members of the fatty acid series with 2 to 6 carbon atoms and their esters.

Ozone can be used as an oxidizing agent for the preparation of either acids or aldehydes and ketones.[55] For example, lignite-tar oil is treated with liquid sulphur dioxide which removes the highly unsaturated compounds but leaves the less saturated compounds. This oil is then cooled until partial solidification takes place and the liquid portion is separated and fractionated. The fraction which boils between 100° and 250° C. at 10 mm. pressure is treated with ozone until the increase in weight amounts to 8 to 12 per cent. This ozonized oil is next hydrolyzed with steam and the acids thus formed are separated with hot concentrated potassium hydroxide solution. On hydrolysis of the resulting soaps, principally palmitic and stearic acids are produced. The oil, after the removal of the acids, is recycled. The total yield of acids amounts to about 18 to 20 per cent of the oil.

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[50] James, U. S. Patent 1,697,653, Jan. 1, 1929; *Chem. Abs.*, 1929, **23**, 1136; Reissue 18,522, July 12, 1932; *Chem. Abs.*, 1932, **26**, 4611. British Patent 209,128, 1922; *J.S.C.I.*, 1924, **43**, 210B. See also Chapter 36.

[51] James, U. S. Patent 1,681,237, Aug. 21, 1928.

[52] See, for example, James, U. S. Patent 1,894,352, Jan. 17, 1933; *Chem. Abs.*, 1933, **27**, 2570; U. S. Patent 1,894,096, Jan. 10, 1933; *Chem. Abs.*, 1933, **27**, 2324.

[53] James, U. S. Patents 1,721,958 and 1,721,959, July 23, 1929; *Chem. Abs.*, 1929, **23**, 4567.

[54] I. G. Farbenindustrie A.-G., British Patent 312,388, 1928; *Chem. Abs.*, 1930, **24**, 861; also French Patent 664,860, 1928; *Chem. Abs.*, 1930, **24**, 860. *Cf.* Andrussov and Dürr, German Patent 542,847, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 2987.

[55] Harries, German Patent 339,562, 1919; *Chem. Abs.*, 1922, **16**, 3486; *J.S.C.I.*, 1922, **41**, 35A.

Aldehydes and ketones formed on treating ozonized oil with steam can be recovered by extraction with potassium hydroxide and then with sodium bisulphite solution. The crystalline bisulphite compounds are treated successively with sodium carbonate and sulphuric acid and the resulting liquid is steam-distilled. Better yields of aldehydes and ketones (up to 80 per cent) may be obtained if the bisulphite treatment is carried out in the presence of potassium bisulphate.

The following method has been suggested[56] for mineral oils which are oxidized only with difficulty. The oils are first refined with sulphuric acid or with liquid sulphur dioxide and then treated with ozone. The ozonides thus formed are removed by adsorption and on treatment with steam, are hydrolyzed to acids.

The electrochemical oxidation of mineral oils to produce acids has been described by Atanasiu,[57] but this is described more completely in Chapter 43.

For converting kerosene and spindle oil to acids, Schrauth[58] proposed to chlorinate the oil to monochloro-derivatives. These are then subjected to fusion with alkalies. The temperature during fusion is first maintained at 200° to 230° C., but during the latter part of the operation, is allowed to rise to 300° C. The product obtained after 6 to 8 hours is a mixture of dry, odorless soaps which are soluble in hot water and lather freely. The excess alkali may be neutralized with hydrochloric acid or fatty acids, or after remelting, the soap may be extracted with steam and water. Hydrogen is evolved during fusion.

For the photochemical oxidation of paraffin oils to fatty acids, a transmission catalyst such as anthraquinone together with an auxiliary catalyst, for example, sodium or potassium hydroxide, calcium hydroxide, adsorptive charcoal which may be impregnated with metallic salts or oxides, or inorganic gels has been proposed.[59]

Acids, together with ketones, have been produced by heating either aliphatic or aromatic hydrocarbons under pressure with carbon monoxide.[60] The catalysts used were the anhydrous chlorides of aluminum and boron. In the presence of aluminum chloride temperatures of 30° to 60° C. are required, but with boron chloride, 180° C. Normal pentane, for example, when treated with carbon monoxide yielded a ketone, boiling at 114° to 116° C., a mixture of ketones boiling at 116° to 250° C., and hexanoic together with other acids.

Alleman[61] obtained acids, melting below —30° C., from the alkali used in washing acid-treated lubricating distillates. The alkali is freed of oil and resins by extraction with gasoline, and the acids are then liberated by hydrolyzing with steam under pressure or by the addition of mineral acids. Further purification results on distilling under reduced pressure. Insoluble salts of these acids can be made by adding soluble metallic salts, such as calcium chloride or nickel sulphate, to the solution of the acids in alkali.

Luther and Klein[61a] produced unsaturated aliphatic acids by distilling the crude oxidation products of higher paraffin hydrocarbons under a pressure of about 8 mm. at 100° to 300° C. in the presence of sulphuric acid, thereby converting the hydroxy fatty acids present into unsaturated acids. The operation may be facilitated by passing an inert gas through the mixture during the distillation.

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[56] Siemens and Halske A.-G., British Patent 263,186, 1925; *Chem. Abs.*, 1928, **22**, 162.

[57] *Bull. chim. soc. romana stiinte,* 1929, **31**, 75; *Chem. Abs.*, 1930, **24**, 2281; Danaila and Atanasiu, German Patent 539,472, 1929; *Chem. Abs.*, 1932, **26**, 1819.

[58] German Patent 327,048, 1914; *Chem. Abs.*, 1921, **15**, 2009.

[59] Vereinigte Chemische Fabriken Kreidl Heller and Co., French Patent 702,183, 1930; *Chem. Abs.*, 1931, **25**, 3919.

[60] Hopff, German Patent 512,718, 1927; *Chem. Abs.*, 1931, **25**, 1258; British Patent 310,438, 1928; *Chem. Abs.*, 1930, **24**, 625; both patents assigned to I. G. Farbenindustrie A.-G.

[61] U. S. Patent 1,694,461, Dec. 11, 1928; assigned to Sun Oil Co.; *Chem. Abs.*, 1929, **23**, 696. See also Chapter 48.

[61a] German Patent 565,481, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 1007.

Chapter 43

Oxidation of Paraffin Wax. Production of Synthetic Fats

It has long been known that when higher paraffins are heated in the presence of air for considerable periods of time they absorb oxygen and become brown in color. Such observations were made at an early date by Bolley[1] and also by Jazukowitsch.[2] The effect of other oxidizing agents on paraffins has also been investigated. Gill and Meusel,[3] for example, studied the action of chromic acid mixtures and Hofstädter[4] and Pouchet,[5] that of nitric acid. Various investigators noted the formation of acetic and other organic acids when air was passed through hot mineral oils.[6]

Schaal[7] was among the first to derive oxidation products in any quantities from petroleum hydrocarbons. He passed a stream of air or oxygen through the heated hydrocarbon in the presence of sodium hydroxide or calcium oxide and thus obtained the salts of the acids. Later, Byerley and Mabery[8] described a process for manufacturing "artificial asphalt" which consisted of blowing air through high-boiling petroleum residues for several days at a temperature of about 230° C. However, as the reaction is exothermic, the temperature often rose much higher. Because of these high temperatures, the final product contained very little oxygen. The oxidation was also probably accompanied by polymerization and condensation of oxygen compounds, such as alcohols and aldehydes. At lower temperatures, however, small proportions of both aliphatic and naphthenic acids were formed.

The production of acids and esters was effected by Gray[9] in "deblooming" petroleum distillates and other hydrocarbons. The process involved the passage of air through the heated hydrocarbons in the presence of ultraviolet light. Various metals or their salts, or porous materials which had been previously impregnated with such substances, were used as catalysts. Ellis[10] also debloomed petroleum distillates by the use of ultraviolet light. In this method, however, oxidation is minimized by the presence of an inert gas such as nitrogen. If the inert gas is not used and oxidation does take place, the oxidation products may be removed afterwards by employing any of the usual methods.

The oxidation of higher paraffins appears to offer a method for the production of high molecular weight aliphatic acids which may be used for the synthesis of fats or in the manufacture of soaps. Oxidation may be effected with air or other oxidizing agents, and with the formation of alcohols and aldehydes very probably as intermediate products. As pointed out in the chapter on the oxidation of methane (Chapter 37), oxidation of high molecular weight hydrocarbons proceeds in steps which seem to be in accord with the hydroxylation theory. In this chapter the oxidation of such hydrocarbons is considered in greater detail.

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[1] *Z. für Chemie*, 1868, 500; *Schweiz. Polyt. Zeit.*, 1868, 13, 65.

[2] *Ber.*, 1875, 8, 768; *J. Russ. Phys.-Chem. Soc.*, 1875, 7, 260.

[3] *Z. für Chemie*, 1869, 65; *J.C.S.*, 1869, 21, 466.

[4] *Ann.*, 1854, 91, 326; *Sitz. k. Ak. Wiss. Wien.*, 1854, 13, 436.

[5] *Ber.*, 1874, 7, 1453; *Compt. rend.*, 1874, 79, 320; *Chem. Soc. Abs.*, 1875, 28, 50.

[6] Zaloziecki, *Z. angew. Chem.*, 1891, 4, 416; Engler and Bock, *Chem. Ztg.*, 1892, 16, 592.

[7] See Chapter 42.

[8] *Amer. Chem. J.*, 1896, 18, 141; *Chem. Soc. Abs.*, 1896, 70 (1), 329.

[9] U. S. Patent 1,158,205, Oct. 26, 1915; *Chem. Abs.*, 1915, 9, 3358.

[10] U. S. Patent 1,089,359, March 3, 1914; assigned to Ellis-Foster Co.

The term "wax acids" appears to be a better designation for these acids than "fatty acids," for it indicates (1) that wax is the source instead of fats, and (2) that these acids differ slightly in their chemical constitution from the true fatty acids. This difference so far as is recognized will be pointed out later.

OXIDATION WITH AIR

Benedix[11] was able to oxidize petrolatum by intimately mixing it with sodium peroxide in the presence of water or with hydrogen peroxide diluted with alkalies or alkaline salts. The reaction was promoted by the presence of alcohol and was completed by heating to 80° C. under pressure. The hydrocarbons were believed to oxidize to acids and these reacted with the alkali present to form soaps.

By passing a current of air through paraffin wax which was kept at a temperature of 290° to 300° C., Schulz[12] obtained principally aldehydes, together with some carbon monoxide and dioxide, and a small quantity of acids.

The use of lower temperatures (100° to 120° C.) during oxidation is recommended.[13] Melted wax is oxidized by a blast of air until a deep yellow color is obtained. Oxidation is then stopped and the product is separated into its oxidized and unoxidized portions. In this way about 70 per cent of the wax was oxidized to oleic and other acids, a ceresin-like wax, aldehydes, and other substances. From the volatile products aliphatic acids and aldehydes were separated. The unoxidized portion may be retreated. A catalyst, such as paraffin wax which has previously been oxidized or mercuric oxide may be used.

Wax acids were obtained by Bergmann[14] by passing air for 15 to 18 days through paraffin wax heated to 130° to 135° C. At the end of that time the product was a brown, unctuous mass, which had an acid number of 132 and formed soaps with alkalies. The acid products were separated from the mass by forming the barium salts. These acids, after being liberated by the use of hydrochloric acid, were further separated by fractional distillation under reduced pressure. The fraction distilling between 270° and 310° C. at 100 mm. pressure was identified as lignoceric acid. From the fraction boiling between 230° and 270° C. two acids were isolated: one melted at 53.7° C., and had the formula $C_{11}H_{22}O_2$ and was unidentified; the other melted at 38.4° C. and was thought to be isopalmitic acid, $C_{16}H_{32}O_2$.

The production of acids from paraffin wax by a similar process of oxidation has also been described.[15] If oxidation is very prolonged a brown resinous substance is obtained which has a possible use in varnish manufacture.

Dovanov[16] treated Grozny paraffin at 160° to 170° C. with air at the rate of 60 to 80 cubic meters per hour for a period of two and one-half hours. He found that the oxidation products had an acid number of 45 to 50, and contained about 10 per cent of water-soluble acids. The larger part were in the form of ethers and could be separated only by saponification followed by fractionation. The dry distillation of their calcium soaps yielded about 22.7 per cent of ketones, of which the largest portion boiled between 65° and 100° C.

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[11] French Patent 446,009, 1912; *J.S.C.I.*, 1913, **32**, 150.

[12] *Eighth Int. Cong. App. Chem.*, 1912, **10**, 273; *Chem. Abs.*, 1912, **6**, 3177.

[13] Chem. Fabrik Troisdorf Dr. Hülsberg and Seiler, Swiss Patent 75,653, 1917; *Chem. Abs.*, 1918, **12**, 222. Schmidt, British Patent 109,386, 1917; *Chem. Abs.*, 1918, **12**, 94; Canadian Patent 223,944, 1922; *Chem. Abs.*, 1922, **16**, 4342.

[14] *Z. angew. Chem.*, 1918, **31**, 69; *Chem. Soc. Abs.*, 1918, **114** (1), 285; *cf.* A.-G. für Mineralöl-Industrie vorm. D. Fanto and Co., *Z. angew. Chem.*, 1918, **31**, 115; *Chem. Soc. Abs.*, 1918, **114** (1), 333.

[15] Bardubitzer Fabrik der A.-G. für Mineralöl-Ind. vorm. D. Fanto and Co., British Patents 131,301, 131,302 and 131,303, 1919; *Chem. Abs.*, 1920, **14**, 135.

[16] *Masloboino-Zhirovoe Delo*, 1932, No. 7, 43; *Chem. Abs.*, 1933, **27**, 3595.

Fischer, Schneider, and Jantsch[17] studied the pressure oxidation of paraffin wax. Their oxidation experiments were carried out in an autoclave equipped with an agitator. Two hundred grams of paraffin wax and 800 cc. of 2.5N sodium carbonate solution were heated to 170° C. while a current of air (200 liters per hour) under 30 atmospheres pressure was passed through the mixture. Oxidation was continued until one-half of the alkali had been neutralized by the wax acids which were formed. The average molecular weight of the acids was 250 and these were found to be insoluble in water and satisfactory for making soap. A considerable quantity of carbon dioxide was formed during the reaction and some decomposition of the sodium salts of the higher wax acids was noted. Light paraffin oils were obtained at the same time.

The influence of various factors was found by these investigators to be as follows: Increased temperature affected the color of the products as well as the speed of oxidation. Increased air pressure accelerated the reaction, and the quantity of air influenced the molecular weights of the acids. Undue prolongation of oxidation resulted in a secondary decomposition. The use of lime instead of sodium carbonate was found to be desirable. Speed of stirring and quantity and concentration of the alkali had little effect. Iron, manganese, and copper were found to be the best catalysts, though cerium, titanium, fuller's earth and charcoal yielded the best-colored products. When the apparatus was lined with lead or glass, the rate of oxidation was retarded although better-colored products were obtained. The addition of aromatic hydrocarbons, such as toluene and xylene, resulted in a greater yield of acids, although neither of these compounds was oxidized under the same conditions in the absence of paraffins. Paraffin wax appeared to be more extensively oxidized when alkalies were not present. Other paraffins, such as those obtained from lignite, coal or peat could be oxidized, though the first two were the more resistant. The yield of wax acids was nearly 75 per cent of the paraffin oxidized.

The solid soaps could be obtained by evaporation of the aqueous solution, or by separating the paraffin and water layers and allowing the latter to stand overnight. During this time the soaps of high molecular weight acids separated as solids. Brown soaps were bleached with sodium hypochlorite or by further treatment in the autoclave at 160° C. The free wax acids were liberated by the addition of a mineral acid or by heating the soap solution with carbon monoxide under pressure. Under such conditions the carbon monoxide acted as formic anhydride, liberating the free acids and forming sodium formate. The wax acids could be further purified by distillation with superheated steam or *in vacuo*. Potassium or mixed potassium and sodium soaps were prepared and all soaps lathered well.

Although the solutions of the sodium salts of lower-molecular weight acids lather well, the presence of such soaps imparts a disagreeable odor to the crude product and makes it hygroscopic. Separation from those of the higher-molecular weight acids is accomplished, as mentioned above, by cooling the alkaline solution and filtering off the solid soaps which precipitate. Evaporation of the filtrate yields soaps of the lower-molecular weight acids. On liberating these from their salts it was found that about one-half, ranging from capric to lauric acid, was insoluble in water.

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[17] Fischer, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 35; Fischer and Schneider, *ibid.*, 1919, 4, 48; Schneider, *ibid.*, 1919, 4, 101; Schneider and Jantsch, *ibid.*, 1919, 4, 118; Schneider, *ibid.*, 1919, 4, 132; Fischer and Schneider, *ibid.*, 1919, 4, 94; *Chem. Abs.*, 1921, 15, 2736, 2737.

At the same time Schneider observed that oxygen-containing compounds, such as alcohols, aldehydes, and ketones, were carried over by the compressed air leaving the autoclave. Such substances were also noted in the cake of residual paraffin. The solid portion of the cake resembled a true wax rather than paraffin.

Attempts were made to identify and separate the wax acids by means of their ethyl esters. The acids all appeared to conform to the general formula $C_nH_{2n}O_2$, and for a large proportion of the acids n was an odd number. On the other hand, the acids from natural fats and oils generally contain an even number of carbon atoms. Schneider also observed that oxidation at ordinary pressure in glass vessels yielded 2 to 3 per cent of acids insoluble in water, but in iron vessels the yield of insoluble acids was 64 per cent. Mercuric oxide showed little catalytic effect.[18] The reaction velocity was much less than that of oxidations conducted under increased pressures. There was some indication that acid anhydrides were formed.

Varmalov[19] also investigated the oxidation of paraffin wax under pressure. One to two hundred grams of Grozny paraffin, melting at 52° C., were mixed with 500 to 1000 cubic centimeters of 2N sodium carbonate solution, and oxidized in an iron autoclave at a temperature of 160° to 180° C. and a pressure of 15 to 30 atmospheres. Air was supplied at the rate of 200 to 400 liters per hour. The results obtained were: (a) the rate of oxidation was directly proportional to the pressure; (b) 20 to 74 per cent of the paraffin was oxidized; (c) wax acids insoluble in water were formed to the extent of 53 to 78 per cent, and soluble acids, 7 to 8 per cent; and (d) the hydroxy-acids were equivalent to 10 per cent of the oxidized paraffin. Wax acids had acid numbers of 172 to 210, and the hydroxy-acids, an ester number of 66.

Holde[20] has shown that the oxidation of paraffins with air at 135° to 145° C. results in the formation of acid anhydrides which are insoluble in 94 per cent alcohol. These anhydrides reacted with 72 per cent alcohol to yield ethyl esters. Possible substitution of esters of glycol and glycerol for natural fats and oils has been suggested.[21]

Montan wax likewise has been oxidized under pressure.[22] This wax was more inert than paraffin wax and the acids formed appeared to undergo decomposition, hence the yield was lower. The soaps from such acids did not lather as well as those made from paraffin wax acids.

By partially oxidizing wax, good yields of alcohols of high molecular weights may be obtained.[23] Catalysts for such oxidations include organic acids of relatively low molecular weight (e.g., formic, acetic, maleic or benzoic acid), or of weak inorganic acids, such as boric acid, antimony pentoxide, or stannic acid. Best results are secured when 5 to 10 per cent of acid is used and the reaction is continued for 2 to 3 hours at temperatures between 100° and 200° C. As an example, hard paraffin wax containing boric anhydride (50 grams per kilogram of wax) is heated to 175° C. and air is passed into the mixture at the rate of 1 cubic meter (containing 16 grams of acetic acid vapor) per hour. At the end of 3 hours a pale-colored oxidation product is obtained which consists of about

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[18] *Cf.* Schmidt, British Patent 109,386, 1917; *Chem. Abs.*, 1918, 12, 94; British Patent 142,507, 1920; *J.S.C.I.*, 1921, 40, 74A.

[19] *Masloboino-Zhirovoe Delo,* 1932, No. 4-5, 41; *Chem. Abs.*, 1933, 27, 3595. An apparatus for the oxidation of paraffin wax under pressure is described by Société Internationales des Combustibles Liquides, French Patent 606,190, 1925; *Brit. Chem. Abs.* **B**, 1927, 464.

[20] *Chem. Ztg.*, 1920, 44, 477; *Chem. Abs.*, 1921, 14, 2724. For the oxidation of petroleum pitch see Holde and Weill, *Petroleum Z.*, 1923, 19, 451; *Chem. Abs.*, 1932, 17, 2497.

[21] Grün, British Patent 160,840, 1921; assigned to G. Schicht A.-G.; *Chem. Abs.*, 1921, 15, 2559.

[22] Fischer and Schneider, *Ges. Abhandl. Kennt. Kohle,* 1919, 4, 180; *Chem. Abs.*, 1921, 15, 2737.

[23] Luther and Dietrich, U. S. Patent 1,931,501, Oct. 24, 1933; assigned to I. G. Farbenindustrie A.-G.; British Patent 353,047, 1930; *Brit. Chem. Abs.* **B**, 1931, 1132.

44 per cent by weight of alcohols. The alcohols can be separated by distillation with steam under pressures less than 100 mm.[24] Mixtures of these alcohols or their boric or stearic esters may be used in coating and polishing compositions.[24a]

Other methods described for the separation of the products obtained by the air oxidation of paraffin wax include that of Pungs.[25] After the oxidation step he warms the mass so that the oxidized portion is obtained as a liquid while the unoxidized portion remains solid. The oxidized portion is further divided into waxes and acids by means of alcohol, the acids being soluble in this solvent. Pataky and Nellensteijn,[26] however, add superheated steam to the air or oxygen and thus distil off the wax acids as they are formed. The distillate separates into a solid layer of wax acids of high molecular weight and a liquid containing soluble acids of low molecular weight.

Besides the catalysts already mentioned, others have been used in the oxidation of paraffin wax. By employing a reduced nickel catalyst, Goswami and Chatterjee[26a] obtained about 20 per cent of higher aldehydes. Kelber[27] converted paraffin wax (m.p. 50° C.), to the extent of about 60 per cent, into wax acids by oxidizing it with air at 130° to 135° C. in the presence of manganese compounds such as the oxide, dioxide and silicate. Osmium trioxide and platinum gauze also accelerated oxidation. Of the wax acids obtained, about 60 per cent were insoluble in water. Some of the water-soluble acids found in the distillate which came over during oxidation were identified as propionic, butyric and valeric, and the insoluble acids contained hexanoic, octanoic, nonanoic, and higher acids. The non-volatile residue was also examined for wax acids. Among the acids isolated from this latter portion were decanoic, myristic, palmitic, stearic and arachidic. Kelber observed that if oxygen was passed in while the paraffin was being heated to 150° to 160° C. some time elapsed before the reaction started, which was accompanied by the evolution of heat. On the other hand, if the paraffin was heated at that temperature for some time and oxygen then passed in, reaction began immediately. This appeared to indicate that oxygen takes no part in the action until a breaking down of the hydrocarbon sets in, whereupon it reacts with the decomposition products.

Franck[28] used 0.5 to 5 per cent of various compounds of lead, mercury, vanadium and chromium as catalysts. He carried out oxidation in an autoclave filled with oxygen at a temperature of 150° C. A series of wax acids, which ranged from acetic to arachidic, was obtained. Upon esterifying a sample of the mixed acids with ethylene glycol, in the presence of 3 per cent of sulphuric acid, a solid fat was formed which possessed the odor of coconut oil. After refining, this product was pale yellow in color.

Contrary to the results of other investigators, Grün, Ulbrick and Wirth[29] found that the oxidation reaction was inhibited by calcium or barium oxides or other compounds having alkaline properties. They believed, however, that acidic substances, such as stearic acid, may be helpful, or at least not show marked inhibitive properties. If the conditions of oxidation are not carefully chosen one carbon atom after another of the intermediate products may be oxidized away, thus producing a whole series of acids which range from formic acid, or even carbon dioxide, to high molecular weight acids. The use of pure oxygen is likely to lead to the formation of explosive peroxides as intermediate products. When oxidation is not too vigorous the product consists of waxes, free acids, alcohols, and unsaponifiable matter. Any hydroxy-acids formed probably react to give esters or estolides[30] or yield unsaturated acids by loss of water. The unsaponifiable matter consists of unchanged paraffin and higher alcohols together with probably aldehydes and ketones. The absence of water appears to promote the formation of acid anhydrides.

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[24] I. G. Farbenindustrie A.-G., British Patent 366,553, 1930; *Chem. Abs.*, 1933, 27, 1890.

[24a] I. G. Farbenindustrie A.-G., British Patent 388,369, 1933; *Chem. Abs.*, 1933, 27, 4642; see also Chapter 45.

[25] German Patent 467,930, 1922; *Chem. Abs.*, 1929, 23, 1748; German Patent 488,877, 1922; *Chem. Abs.*, 1930, 24, 2323; both patents assigned to I. G. Farbenindustrie A.-G.

[26] British Patent 239,178, 1924; *Chem. Abs.*, 1926, 20, 2084; U. S. Patent 1,627,452, May 3, 1926; *Chem. Abs.*, 1927, 21, 2196.

[26a] *J. Indian Chem. Soc.*, 1931, 8, 533; *Chem. Abs.*, 1932, 26, 693.

[27] Kelber, *Ber.*, 1920, 53, 66, 1567; *Chem. Abs.*, 1920, 14, 2343.

[28] *Chem. Ztg.*, 1920, 44, 309; *J.S.C.I.*, 1920, 39, 395A.

[29] *Ber.*, 1920, 53, 987; *Chem. Abs.*, 1920, 14, 3416. See also G. Schicht A.-G., British Patent 183,186, 1921; *Chem. Abs.*, 1923, 17, 221; British Patent 148,291, 1920; *Chem. Abs.*, 1921, 15, 605.

Collin[31] was unable to identify any of the acids in paraffin wax which had been oxidized on a "commercial scale." He concluded, however, that it contained about 80 per cent saturated acids ranging in molecular weight from 145 to 300, and that probably half of the acids had a molecular weight corresponding to acids of 14 carbon atoms or less. No one acid was present in any predominating quantity.

Despite the fact that the presence of certain alkaline substances may be detrimental to the oxidation, certain processes have been developed which depend upon the use of such substances. Paraffin, petrolatum and naphthenes can be oxidized with air at 150° C. for 24 to 36 hours in the presence of about 2 per cent of a light metal such as sodium, potassium or magnesium.[32] Over 20 per cent of the hydrocarbons are converted into acids, the salts of which can be employed as soaps. Plauson and Vielle[33] obtained soaps by oxidizing paraffin at 125° to 150° C. with air or oxygen under 5 to 10 atmospheres pressure in the presence of an alkali. The volatile products, amounting to 16 to 18 per cent of the paraffin, are withdrawn and condensed. About 60 to 70 per cent of the paraffin is changed into saponifiable matter, and the remaining non-volatile portion can be emulsified in the soap. When air is the oxidizing agent it should be free of both moisture and carbon dioxide.

The salts of organic acids also appear to function well as catalysts. These include salts of the alkaline earth metals, such as barium stearate or calcium cinnamate, in the absence of free alkalies or alkaline earths.[34] Similarly, manganese and zinc stearate,[35] manganese acetylacetonate,[36] or naphthenate[36a] or other metallic enolates have been used. Nitrogenous bases,[37] e.g., hexamethylenetetramine, aniline and butylamine, may be used in conjunction with such salts as manganese or cerium stearate.

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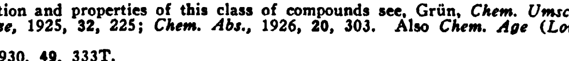
[30] Estolides are the esters formed by the interesterification of high molecular weight hydroxy-acids. For example, an estolide has been obtained from 12-hydroxy-stearic acid by the interesterification of three molecules.



$$3C_{17}H_{34}\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown COOH} \longrightarrow C_{17}H_{34}\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown COOC_{17}H_{34}COOC_{17}H_{34}COOH} + 2H_2O$$

For the preparation and properties of this class of compounds see, Grün, *Chem. Umschau Fette, Oele, Wachse u. Harze,* 1925, 32, 225; *Chem. Abs.*, 1926, 20, 303. Also *Chem. Age* (*London*), Mar. 24, 1928, 262.

[31] *J.S.C.I.*, 1930, 49, 333T.

[32] Farbenfabrik vorm. F. Bayer und Co., German Patent 346,520, 1917; *J.S.C.I.*, 1922, 41, 270A.

[33] British Patent 156,141, 1920; *Chem. Abs.*, 1921, 15, 1826; also French Patent 533,577, 1921. *Cf.* I. G. Farbenindustrie A.-G., British Patent 366,997, 1930; *Chem. Abs.*, 1933, 27, 1895; Friedolsheim and Luther, German Patent 564,433, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 991.

[34] I. G. Farbenindustrie A.-G., British Patent 310,069, 1927; *Brit. Chem. Abs.* B, 1929, 636.

[35] Zerner, *Chem. Ztg.*, 1930, 54, 257, 279; *Brit. Chem. Abs.* B, 1930, 543.

[36] I. G. Farbenindustrie A.-G., British Patent 303,268, 1927; *Brit. Chem. Abs.* B, 1929, 163.

[36a] I. G. Farbenindustrie A.-G., British Patent 347,620, 1930; *Chem. Abs.*, 1932, 26, 2747.

[37] Hofmann, U. S. Patent 1,762,688, June 10, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, 24, 3798. See also British Patent 298,704, 1927; *Chem. Abs.*, 1929, 23, 3078. Dunkel, German Patent 522,361, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 3011.

Among the inorganic catalysts, metallic borates,[38] cupric oxide[39] and manganites and manganates[40] have been mentioned for the oxidation of paraffin wax with either oxygen or air. Neutral or acid alkali halides or oxalates (sodium chloride or sodium oxalate) have been suggested, particularly for the oxidation of montan wax.[41]

USE OF OTHER OXIDIZING AGENTS

Paraffin wax, melting at 50° to 52° C., can be oxidized with air containing 2 per cent nitrogen dioxide[42] at temperatures which range from 110° to 150° C. Complete conversion of the paraffin into oxidation products is possible in all cases, the time for such action, however, varying inversely with the temperature. The products were not excessively discolored, and consisted of a mixture of acetic, butyric and higher acids and about 15 per cent of unsaponifiable oil. With pure nitrogen dioxide at 140° C., oxidation was complete in a much shorter time, and the exit gas consisted principally of nitric oxide, together with small quantities of nitrogen, hydrogen cyanide, and carbon monoxide. As the alkaline solutions of the oxidized wax were red when nitrogen dioxide was used, this was taken as evidence that some nitro-compounds were formed.

Gränacher observed that when pure n-undecane was treated with nitrogen dioxide at 140° C., the product was a mixture of acids, none of which was higher than nonanoic acid. Only about 60 per cent of the hydrocarbon was oxidized. Since paraffin waxes were more completely and quickly changed to acids than was undecane (a straight-chain hydrocarbon), Gränacher concluded that paraffin wax consisted chiefly of branched-chain hydrocarbons.

In some further work on the oxidation of paraffin with nitrogen dioxide, it was impossible to detect either stearic or palmitic acid.[43] The crude acids were extracted with sodium hydroxide solution, converted into the barium salts to remove neutral products, and the free acids were then liberated. The ethyl esters of these acids were made and separated by distillation into two fractions, the first boiling at 37° to 240° C. (at 23 mm), and the second at 240° to 300° C. (at 23 mm). From the second fraction the acid $C_{22}H_{44}O_2$ (m.p. 59° to 60° C.) was obtained. This acid differed greatly from behenic acid ($C_{22}H_{44}O_2$), which further substantiated the belief that paraffin wax contains considerable quantities of hydrocarbons other than normal straight-chain ones. In a second experiment the esters were separated into fractions which boiled at 90° to 135° C. and 135° to 155° C. at 12 mm pressure. From the first fraction was obtained the acid $C_{14}H_{28}O_3$ and from the second, the acid $C_{15}H_{30}O_3$. These were saturated, liquid hydroxy-acids, and probably contained a naphthenic or branched-chain structure.

The oxidation of melted paraffin wax at 60° C. with liquid nitrogen tetroxide under 4 atmospheres pressure leads to a product containing only 12 per cent unsaponifiable matter.[44] During oxidation the nitrogen tetroxide is reduced to nitric oxide. This gas, however, may be mixed with oxygen to re-form the tetroxide which can be used again. By making the working conditions milder as the reaction proceeds the formation of hydroxy-acids[45] can be largely prevented. Thus, crude paraffin may be oxidized with a mixture of nitrogen oxides in three stages at 110°, 90°, and 60° C., respectively, and the product will have less than 10 per cent hydroxy-acids. The gases, together with the partly oxidized wax, are passed from one autoclave to the next. The first autoclave is fed with nitrogen dioxide and this subsequently becomes diluted with nitric oxide as the reaction proceeds. Decreasing the pressure or velocity of the gases is of aid. Zinc or aluminum stearate, or metallic phosphates may be used as catalysts.

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[38] Klein, German Patent 502,433, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, 24, 4789.

[39] Steopoe, *Bull. chim. soc. romana stiinte*, 1924, 27, 11; *Chem. Abs.*, 1927, 21, 1795.

[40] Klein, German Patent 570,130, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 2454.

[41] Hellthaler and Peter, German Patent 523,518, 1928; assigned to A. Riebeck'sche Montanwerke A.-G.; *Chem. Abs.*, 1931, 25, 3822. Luther and Fleming, U. S. Patent 1,874,322, Aug. 30, 1932; assigned to I. G. Farbenindustrie A.-G.; also British Patents 386,715 and 386,725, 1931; *Brit. Chem. Abs.* B, 1933, 260.

[42] Gränacher, *Helv. Chim. Acta*, 1920, 3, 721; *Chem. Abs.*, 1921, 15, 668.

[43] Gränacher and Schaufelberger, *Helv. Chim. Acta*, 1922, 5, 392; *Chem. Abs.*, 1923, 17, 2864.

[44] I. G. Farbenindustrie A.-G., British Patent 324,492, 1928; *Chem. Abs.*, 1930, 24, 3354; *cf.* French Patent 672,936, 1928; *Chem. Abs.*, 1930, 24, 2285.

Other catalysts which have been used in the oxidation of paraffin wax with the oxides of nitrogen are barium stearate, calcium and barium cinnamate, and similar organic compounds of the alkaline earth metals, magnesium and aluminum,[46] and also barium and manganese acetylacetonates.[47]

After paraffin wax has been oxidized with the higher oxides of nitrogen, the crude acids can be purified by heating or distilling below 300° C. with carbon monoxide or hydrogen in the presence of a hydrogenating catalyst[48] or by treatment with alkalies.[48a] In this way the nitrogen-containing fatty acids are either reduced or the nitrogen is split off.

Schaarschmidt and Thiele[49] obtained acids by oxidizing unsaturated compounds (made from the chlorine derivatives of paraffin) with potassium permanganate. Chlorine was passed into molten paraffin at 160° C. through a Witt stirrer which was rapidly rotated. Reaction proceeds almost to completion without the aid of external heat. Hydrogen chloride was then eliminated either by heating the products to 300° C. or with alcoholic potassium hydroxide, the latter method yielding olefins of higher iodine number. The olefins thus obtained were then oxidized with potassium permanganate. For example, an olefin having a bromine number of 24 and derived from a chloroparaffin containing 10.6 per cent chlorine, on oxidation with potassium permanganate yielded the acid $C_{14}H_{29}COOH$. The more unsaturated the olefin, the greater and quicker the absorption of oxygen.

Since the ease with which these water-insoluble unsaturated compounds can be oxidized depends on their state of subdivision, the following modifications of the oxidation procedure were tried: (1) The olefin was emulsified with an aqueous solution of sodium palmitate and an aqueous solution of permanganate was added. Oxidation was stopped when the weight of permanganate used was about six times the weight of olefin. (2) The reaction was started with a small quantity of sodium palmitate and olefin, and further additions of the latter were made as the permanganate became reduced. The quantities of acids and of unsaponifiable material were about the same by both methods. The acid values of the products obtained by the second method, however, were greater than those obtained by the first. Oxidation by means of permanganate apparently does not stop with the splitting of the double bonds, but also further changes a large portion of the cleavage products, as a quantity of water-soluble acids was formed, and also a large portion of the olefin was oxidized to carbon dioxide.

Ozone is readily absorbed by the olefins, the amount corresponding closely to the quantity of hydrogen chloride split off in the preparation of the olefin. The ozonides can be decomposed with water and the non-acid aldehyde portions further oxidized with ozone. In this manner, 105 grams of higher fatty acids, together with a considerable amount of water-soluble acids, were obtained from 150 grams of olefins. The latter were made from a chloroparaffin (containing 19.4 per cent chlorine) by means of alcoholic potassium hydroxide.

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[45] I. G. Farbenindustrie A.-G., British Patent 327,707, 1929; *Brit. Chem. Abs.* **B**, 1930, 599. *Cf.* French Patent 715,327, 1931; *Chem. Abs.*, 1932, **26**, 2045; French Patent 735,297, 1932; *Chem. Abs.*, 1933, **27**, 1007.

[46] I. G. Farbenindustrie A.-G., British Patent 310,069, 1927; *Chem. Abs.*, 1930, **24**, 625. See also French Patent 677,859, 1929; *Chem. Abs.*, 1930, **24**, 3247; British Patent 364,574, 1930; *Brit. Chem. Abs.* **B**, 1932, 313.

[47] Luther and Willfroth, U. S. Patent 1,788,799, Jan. 13, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 1070.

[48] I. G. Farbenindustrie A.-G., British Patent 342,670, 1929; *Chem. Abs.*, 1931, **25**, 4283; French Patent 697,595, 1930; *Chem. Abs.*, 1931, **25**, 3015.

[48a] I. G. Farbenindustrie A.-G., French Patent 713,383, 1931; *Chem. Abs.*, 1932, **26**, 1621.

[49] *Ber.*, 1920, **53**, 2128; *Chem. Abs.*, 1921, **15**, 1309.

The electrochemical oxidation of paraffins (which melted from 38 to 53° C.), after thorough refining with 98 per cent sulphuric acid, was studied by Atanasiu.[50] The apparatus used consisted of a cylindrical container of sheet lead, which served as the anode, and a porcelain cell into which dipped a lead cathode. The electrolyte was 20 per cent sulphuric acid (d. 1.2). The paraffins are relatively easily oxidized, particularly in the presence of a catalyst such as 5 per cent potassium dichromate or better, 4 per cent ceric sulphate. Since the oxidation proceeds slowly, the higher yields are obtained with low current densities. The reaction appears to be essentially chemical as the catalyst is alternately reduced and electrochemically reoxidized. The products are wax acids, unsaponifiable matter, water and carbon dioxide. The character of wax acids so obtained varies with the nature of the paraffin, the acid value of the products being about 150 for a paraffin which melted at 37° C. and about 200 for one which melted at 50° C. Soft paraffins are generally the more easily oxidized, but the products contain a large quantity of unsaponifiable material and resins which are difficult to separate.

Grün and his collaborators[51] found that oxidation of paraffin at 160° C. took place to about the same extent in the presence or absence of ultraviolet light. On the other hand, an increase in the quantity of air used, or in the time, gave a large yield of acids. The presence of moisture appears to affect the yield also, though the data on this point were not conclusive. Carbon monoxide, however, retards oxidation. With air diluted with carbon dioxide it was shown that oxidation takes place even when the mixture contains as little as 1.3 per cent by weight of oxygen.

The action of ozone on paraffin and montan waxes was investigated by Fischer and Schneider.[52] The wax was dissolved in acetylene tetrachloride and ozonized for 24 hours at 50° to 60° C. and the quantity of acid products insoluble in water was determined. From preheated montan wax, hard paraffin wax, or lignite tar very little wax acids were obtained. On the other hand, the yields of such acids from paraffin wax of low-temperature tar, from montan wax (not preheated), and from ozokerite were large. These differences were ascribed to the relative proportions of straight- and branched-chain hydrocarbons in the waxes, the latter class being more easily attacked by the ozone.

MISCELLANEOUS OXIDATION REACTIONS

The three constituents of lignite tar, namely, tar oil, paraffin and montan wax, have been oxidized with oxygen in the presence of dilute sodium carbonate solution by Schneider.[53] The tar oil, after the removal of phenols and solid paraffins, consisted of approximately 50 per cent unsaturates, 30 to 40 per cent naphthenes, and 10 per cent paraffin hydrocarbons. When oxidized with air at 200° C. under 30 atmospheres pressure, in the absence of carbonate solution, about half was precipitated as solid asphalt and the remainder gave on distillation a light yellow liquid. In the presence of the carbonate solution no solid product was formed, but about 55 per cent was changed to an alkali-soluble, syrupy liquid (insoluble in petroleum ether) which had a specific gravity greater than 1.0. This seemed to indicate that the product was not an aliphatic acid, but something similar to Charitschkov's polynaphthenic acids.[54]

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[50] *Ber.*, 1931, **64B**, 252; *Brit. Chem. Abs.* **A**, 1931, 460; *Bull chim. soc. romana stiinte*, 1929, **31**, 75; *Chem. Abs.*, 1930, **24**, 2281; *ibid.*, 1931, **25**, 2277. See also Danaila and Atanasiu, German Patent 539,472, 1929; *Chem. Abs.*, 1932, **26**, 1819.

[51] Grün and Wirth, *Z. angew. Chem.*, 1920, **33**, 291; *Chem. Abs.*, 1921, **15**, 1071; Grün and Ulbrich, *Z. angew. Chem.*, 1923, **26**, 125; *Chem. Abs.*, 1923, **17**, 1782.

[52] *Ges. Abhandl. Kennt. Kohle*, 1920, **5**, 117; *Chem. Abs.*, 1923, **17**, 2497.

[53] *Brennstoff-Chem.*, 1920, **1**, 70, 80; *Chem. Abs.*, 1921, **15**, 743.

Oxidation of the lignite paraffin, which melted at 53° C., led to the following conclusions: (1) deep-seated oxidation with the formation of low molecular weight acids does not take place; (2) alcohols and aldehydes are formed only in traces while acids are formed almost exclusively; (3) the acids are monobasic wax acids, and their solubility in petroleum ether indicates the absence of any appreciable quantities of hydroxy-acids; (4) dibasic acids, such as oxalic, are formed only in minute quantities; and (5) the oxidation seems to consist of the formation of acids of high molecular weight, the loss of carbon dioxide, followed by re-oxidation. In this way a homologous series of acids is formed.

As found with paraffin wax from other sources, an increase in temperature of 10° C. appeared to double the reaction velocity and an increase in the oxygen concentration also speeded up the reaction. At a given temperature the quantity of wax acids produced increased with the time allowed for oxidation. Salts of iron, copper and manganese accelerated the reaction, but the salts of nickel, cobalt, chromium, lead, mercury, cerium, titanium and vanadium and also charcoal appeared to have no effect. The acids which were isolated varied from $C_{13}H_{26}O_2$ to $C_{19}H_{38}O_2$, all apparently having an odd number of carbon atoms. The sodium soaps, which separated directly from the reaction products, possessed good lathering and detergent qualities.

Fischer, Schrader and Friedrich[54a] subjected lignin dissolved in dilute sodium carbonate to prolonged oxidation with air at 200° C. under a pressure of 55 atmospheres, obtaining an orange-colored solution which contained 12.8 per cent of the carbon originally present. This liquid on acidification and distillation with steam, gave fatty acids and 0.06 per cent of benzoic acid. The non-volatile acids were extracted with ether and their barium salts were separated by fractional crystallization. Acids from the more soluble barium salts consisted of isophthalic and benzenetricarboxylic acids. The slightly soluble barium salts yielded anhydrides of succinic, phthalic and trimellitic acids and the insoluble salts on acidification yielded oxalic and fumaric acids in solution and benzenetri- and benzenepentacarboxylic, mellitic, prehnitic and hemimellitic acids as precipitates. A yield of 8.28 per cent of aliphatic acids and 3.12 per cent of benzenecarboxylic acids was obtained.

Langer[55] carried out some experiments, which were rather qualitative than quantitative, on the oxidation of petrolatum oils and liquid and solid paraffins. Although some indications were obtained that acids were formed, no individual acid was identified. The oxidizing agents used were: potassium permanganate in alkaline and acid solutions, sodium hypochlorite, manganese dioxide and hydrochloric acid, nitric acid, and potassium dichromate with hydrochloric acid.

The oxidation product from solid paraffin resembled a salve. With litharge it formed lead salts which were soluble in ether. This indicated that acids of the oleic type were formed. From petrolatum, hard and soft resins were produced, the latter containing no substances of an acid character. The yield of saponifiable matter was less than with petrolatum oil and no soluble lead salts were formed.

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[54] See Chapter 48.

[54a] *Ges. Abhandl. Kennt. Kohle,* 1921, 6, 1; *Chem. Abs.,* 1924, 18, 2331; Fischer, Schrader and Treibs, *Ges. Abhandl. Kennt. Kohle,* 1921, 5, 221; *Chem. Abs.,* 1923, 17, 2557.

[55] *Chem. Ztg.,* 1921, 45, 466; *Chem. Abs.,* 1921, 15, 2717.

Yellow petrolatum oils on oxidation yielded a supernatant liquid and a sludge. From the solution of this sludge in dilute sulphuric acid was obtained an oil only slightly soluble in dilute sodium carbonate or hydroxide solutions. When heated on a water bath with concentrated sulphuric acid, sulphur dioxide was evolved and a crystalline mass insoluble in all ordinary solvents was obtained. Despite careful removal of all sulphuric acid, this latter product gave sulphur dioxide on burning. The supernatant liquid from the oxidation of petrolatum oil showed a similar behavior.

On heating liquid paraffin with oxygen under pressure Tschernozhukov[56] obtained oxygenated compounds which were free of sulphur. Neither asphaltenes nor carbenes were formed. Crude Balakhani, Grozny, and Emba oils, under the same conditions, however, yielded asphaltenic sediments, having formulas such as $C_{136}H_{142}O_{12}S$ and $C_{172}H_{176}O_{14}S$. Asphalt-like substances were also obtained when the white oils from Baku and Emba crudes were heated with sulphur and then oxidized. When the sulphur-treated oils were heated with sulphuric acid, sulphur dioxide was liberated. Tschernozhukov concluded from these experiments that asphaltenes were formed from crude oil by unknown sulphur compounds in the various stages of oxidation.

In the oxidation of ordinary paraffin wax in the presence of manganese dioxide or fuller's earth only normal aliphatic acids are obtained. This indicates that paraffin contains only normal aliphatic hydrocarbons which is in direct contrast to Gränacher's[57] conclusion. If ceresin (protoparaffin) contained naphthenes, then naphthenic acids, which could be separated from the aliphatic acids, should be produced also. To verify this, Marcusson[58] oxidized ceresin (melting point 68° to 71° C.) with oxygen for 35 hours at 125° C., and then for 55 hours at 150° C., with manganese dioxide deposited on fuller's earth as a catalyst. The product was separated into saponifiable and unsaponifiable portions according to the method of Hönig and Spitz,[59] and the acids were divided into solid and liquid fractions by the application of Varrentrapp's[60] lead salt method. The unsaponifiable material, which amounted to about 44 per cent of the ceresin used, consisted largely of saturated and unsaturated hydrocarbons, ketones and alcohols. The liquid acids were obtained as a thick oil, with an acid number of 115, iodine number of 11 and a density less than 1. They were considered a mixture of polymerized unsaturated acids. The solid acids melted at 60° to 62° C., had an acid number of 146, and an apparent molecular weight of 346. They were extremely soluble in the usual solvents, such as benzene and alcohol, which is typical of branched-chain compounds. It was therefore concluded that ceresin consists principally of branched-chain hydrocarbons.

A mixture of various paraffinic substances can also be oxidized to yield acids which may be employed in the manufacture of soaps. Thus, Schrauth and Friesenhahn[61] used a mixture of 300 kg. of paraffin wax, 350 kg. of beeswax, 300 kg. of ceresin, 30 kg. of sodium hydroxide, and 100 liters of water. The mixture was heated for 8 hours at 160° to 180° C., with brisk agitation, and a pressure of 10 atmospheres of air or oxygen was maintained. A catalyst was not necessary. The use of sodium carbonate in place of sodium hydroxide is to be avoided, as the former gives rise to the formation of anhydrides, lactones, or waxy substances, all of which reduce the detergent property of the soap. After heating, the product is withdrawn and mixed with water, coloring matter and perfume. This finished product lathers freely, and contains only 15 to 25 per cent unsaponifiable material, which however is readily emulsified.

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[56] *Neft. Khoz.*, 1928, 15, 670; *Brit. Chem. Abs.* B, 1929, 584.

[57] Gränacher, *Helv. Chim. Acta*, 1920, 3, 721; *Chem. Abs.*, 1921, 15, 668.

[58] *Chem. Ztg.*, 1925, 49, 166; *Chem. Abs.*, 1925, 19, 3081.

[59] *Z. angew. Chem.*, 1891, 4, 565; *Chem. Soc. Abs.*, 1893, 64 (2), 102. See Ubbelohde, "Handbuch der Chemie und Technologie der Öle und Fette," S. Hirzel, Leipzig, 1908, 1, 259.

[60] *Ann.*, 1840, 35, 196. See Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan and Co., New York, 1913, 1, 543.

[61] *Chem. Ztg.*, 1921, 45, 177; *J.S.C.I.*, 1921, 40, 226A.

OTHER METHODS FOR OXIDIZING PARAFFINS

A brief review of some other industrial methods for oxidizing the paraffinic hydrocarbons and also for separating the products of oxidation follows:

By spraying the liquid hydrocarbons into the top of a cylindrical vessel and injecting oxygen or air at the bottom, thus securing an intimate mixture of the two reacting materials, the time required for oxidation can be greatly reduced. In one process, the vessel is kept at 80° C., and packed with a filling material such as pumice stone, which may also be impregnated with a catalyst. Substances which can be used as catalysts are the oxides of copper, nickel, and manganese.[62]

Instead of spraying the paraffin into air, Reid and Burke[63] oxidized molten paraffin by treating it with air comminuted and disseminated throughout the mass in such an extreme degree of subdivision as to approach molecular dispersion. In this way the speed of the reaction at any given temperature is greatly accelerated. This subdivision of the air is accomplished by high-speed stirrers, such as a Witt stirrer. As an example, a 60 per cent conversion of paraffin wax to wax acids was obtained by oxidizing at 175° C. under 150 lbs. per sq. in. pressure and with the stirrer rotating at 3000 r.p.m. The use of solutions of alkalies, such as sodium carbonate or hydroxide, is also recommended.

Molten paraffin, or hydrocarbons such as ceresin, petrolatum, or paraffin oils, which have been refined with liquid sulphur dioxide, are oxidized[64] with a current of air in vessels containing some filling material. This material may consist of rings or cones of a non-porous nature and may or may not be catalytic. For non-catalytic material, glass or porcelain can be used, and iron or manganese serve as catalytic materials. The use of aluminum or its alloys as filling materials is said to aid in controlling the temperature. The filling extends far above the liquid level so as to help the oxidizing action of the air on the foam or spray carried over by the air. The temperature is maintained between 160° and 180° C. In this manner there is obtained a partial separation of oxidized and unoxidized hydrocarbons. A clear, yellow oxidation product results which is of use in soap manufacture. The process can also be carried out under pressure, or in the presence of inert solvents. Montan wax,[65] either alone or mixed with paraffin hydrocarbons, can be oxidized in the same manner.

Another method for the production of wax acids, anhydrides, aldehydes, alcohols and ketones from paraffins provides for the purification of the hydrocarbons by treatment with hydrogen at 5 to 500 atmospheres pressure at 150° to 450° C.[65a] Sulphur compounds are thus removed and any unsaturated compounds hydrogenated.

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[62] Deutsche Erdöl A.-G., British Patent 148,892, 1920; *J.S.C.I.*, 1921, **40**, 729A.

[63] U. S. Patent 1,663,524, March 20, 1928; assigned to E. I. duPont de Nemours and Co., Inc.

[64] Mittasch and Luther, German Patent 405,850, 1921; assigned to Badische Anilin- und Soda-Fabrik; *J.S.C.I.*, 1925, **44**, 179B; French Patent 552,416, 1923. Pungs, German Patent 489,936, 1922; *Chem. Abs.*, 1930, **24**, 2285; Luther, German Patent 434,923, 1922; *Brit. Chem. Abs.* **B**, 1927, 291; both patents assigned to I. G. Farbenindustrie A.-G.

[65] Pungs, German Patent 407,245, 1922; *J.S.C.I.*, 1925, **44**, 492B; this patent is an addition to German Patent 405,850, 1921, to Mittasch and Luther; *J.S.C.I.*, 1925, **44**, 179B; both patents assigned to Badische Anilin- und Soda-Fabrik.

[65a] I. G. Farbenindustrie A.-G., British Patent 363,711, 1930; *Chem. Abs.*, 1933, **27**, 1638; *cf.* Haslam, U. S. Patent 1,904,452, Apr. 18, 1933; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 3598; Haslam, British Patent 369,852, 1930; assigned to Standard-I. G. Co.; *Chem. Abs.*, 1933, **27**, 2293.

Utilization of the heat developed during the reaction for the preheating of a fresh charge of hydrocarbon has been proposed by Luther.[66] A process developed by Luther and Goetze[67] provides that the foam drawn off at the top of the reaction vessel be further oxidized by returning it to the bottom of the same vessel or by passage through other vessels connected in series.

Mathesius[68] recommended the use of relatively large quantities of water, high pressures, and also alkalies to unite with the acids and prevent further decomposition. Schaffner[69] found that emulsifying the hydrocarbon with a water solution of an aliphatic or aromatic sulphonic acid, aids in the oxidation of the hydrocarbon. Luther and Wille[70] prevented the formation of resinous by-products in the oxidation of paraffin oils and waxes by stopping the reaction before all of the initial products have been oxidized. They extracted the oxidized portion with methyl alcohol, and resubjected the unoxidized residue to oxidation. Fresh unoxidized material can be added after each extraction with alcohol.

In another method for the oxidation of hydrocarbon waxes only a portion of the initial material is oxidized and reaction is stopped before discoloration occurs.[71] The oxidation products can then be removed by distillation. The non-oxidized portion is mixed with fresh material and oxidation repeated. Such a process can be operated in a continuous manner. Scanlin[72] proposed to oxidize paraffin wax at 290° to 330° F. (140° to 165° C.) until the product has an acid value of 35. The oxidized and unoxidized portions are then separated by sweating. The unoxidized portion is added to fresh stock and oxidized again. The oxidized portion is used for making soaps, or for compounding with lubricating oils.[73] By this process the formation of gummy oxidation products insoluble in hydrocarbon oils is avoided.

The hydroxy-acids present in the crude oxidation products of paraffin and montan wax, when distilled under reduced pressures in the presence of carbon dioxide or steam, are converted into long-chain unsaturated acids.[74] Catalysts such as red phosphorus, metallic oxides, or sulphuric acid can be employed in the distillation.

Light-colored products may also be obtained from paraffin and montan wax by oxidizing with air or oxygen at 120° to 180° C. in the presence of small quantities of aqueous non-oxidizing strong acids, or of an ansolvo-acid.[75] Such catalysts may be, 0.1 per cent of 45 per cent sulphuric acid, 0.1 per cent oxalic acid, or 0.3 per cent of the ansolvo-acid obtained from zinc chloride and acetic acid, $(ZnCl_2.2C_2H_3O_2)H_2$. These products can be used as substitutes for beeswax.

Schmidt and Grün,[76] on the other hand, produce a light-colored wax from paraffin by shortening the time of heating. For example, paraffin wax which melts at 50° C. is mixed with a little stearic acid and heated for 6 to 8 hours at

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[66] German Patent 490,249, 1923; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 2137. See also I. G. Farbenindustrie A.-G., British Patent 25[illegible]099, 1925; *Brit. Chem. Abs.* **B**, 1926, 987. British Patent 337,130, 1929; *Brit. Chem. Abs.* **B**, 1931, 147.

[67] German Patent 526,001, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 4328. See also British Patent 309,206, 1927; *Brit. Chem. Abs.* **B**, 1929, 459.

[68] German Patent 350,621, 1916; *J.S.C.I.*, 1922, **41**, 728A.

[69] German Patent 377,815, 1920; *J.S.C.I.*, 1923, **42**, 1032A.

[70] German Patent 524,354, 1925; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 3664.

[71] I. G. Farbenindustrie A.-G., British Patent 324.189, 1928; *Brit. Chem. Abs.* **B**, 1930, 314; French Patent 680,351, 1929; *Chem. Abs.*, 1930, **24**, 3798.

[72] U. S. Patent 1,668,871, May 8, 1928; assigned to Texas Co. See also Gallsworthy, U. S. Patent 1,909,945, May 23, 1933; assigned to Texas Co.; *Chem. Abs.*, 1933, **27**, 4071.

[73] MacKenzie and Haskell, U. S. Patent 1,705,298, Mar. 12, 1929; assigned to Texas Co.; *Chem. Abs.*, 1929, **23**, 2030.

[74] I. G. Farbenindustrie A.-G., British Patent 322,437, 1928; *Chem. Abs.*, 1930, **24**, 2909; French Patent 676,088, 1929; *Chem. Abs.*, 1930, **24**, 2758; British Patent 365,613, 1930; *Brit. chem. Abs.* **B**, 1932, 299.

[75] I. G. Farbenindustrie A.-G., British Patent 324,903, 1928; *Brit. Chem. Abs.* **B**, 1930, 406.

[76] German Patent 385,375, 1919.

150° to 155° C. Contact substances such as the oxides or salts of lead, manganese, nickel, cobalt, cerium or thorium may also be used. At the end of the operation the mass is extracted with alcohol and the wax is obtained as an insoluble product. The wax is a light yellow, opaque substance which melts at a temperature just slightly higher than the original material.

Another method of making light-colored products consists in reducing the temperature, pressure, rate of flow of gas, or concentration of oxidizing agent as reaction proceeds.[76a]

SEPARATION OF OXIDIZED FROM UNOXIDIZED MATERIALS

In the preceding text, reference has been briefly made to procedures for the separation of oxidized from unoxidized wax. From this it has been seen that a number of methods are available. These may be roughly classified as (1) sweating, (2) extraction with alkalies, (3) separation with solvents. Combination of the methods may of course be used.

Attention has already been called to sweating as a method of separating the crude acids, as liquids, from the unoxidized solid products.[77] The crude acids, moreover, can be further purified by sweating or pressing them at temperatures slightly below their melting points.[78]

The use of alkalies, however, permits a much greater variation in the separation of the products of oxidation. For example, the crude products may be saponified with sodium hydroxide, and after extracting with water the acids can be set free by the addition of a mineral acid;[79] or, after saponification, the unsaponifiable bodies may be obtained by sweating and pressing operations.[80]

The soap solution obtained by the saponification of the crude oxidation product may be treated before the free acids are liberated to separate the saponifiable from the unsaponifiable matter. This may be done by emulsifying it with light petroleum or other solvent and then centrifuging[81] or the solution may be cooled to 15° C. or lower to effect separation of the unsaponifiable portion.[82] A similar method consists in treating the saponified products with a methanol-water mixture, to which is then added benzine. Two layers are formed, one of which is a soap solution of water-alcohol, and the other a solution of unsaponified material in benzine.[82a]

The acids in the oxidation products can be saponified with the alkaline earths, magnesia,[83] anhydrous sodium carbonate[84] or ammonium carbonate.[84a] The salts thus obtained are dried and purified by extraction with benzine. The free acids may then be liberated by the addition of sulphuric or other mineral acid. These free acids can be further purified and decolorized by subjecting them at 12° to 13° C. to a pressure of 100 atmospheres in a hydraulic press.[85]

[76a] I. G. Farbenindustrie A.-G., German Patent 576,003, 1933; *Chem. Abs.*, 1933, **27**, 3720.

[77] Pungs, German Patents 467,930 and 488,877, 1922; both assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1929, **23**, 1748; 1930, **24**, 2323.

[78] I. G. Farbenindustrie A.-G., French Patent 672,105, 1929; *Chem. Abs.*, 1930, **24**, 2285; British Patent 321,399, 1928; *Chem. Abs.*, 1930, **24**, 2909.

[79] Franzen and Luther, German Patent 489,938, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, **24**, 2142.

[80] Luther and Franzen, German Patent 518,389, 1927; *Chem. Abs.*, 1931, **25**, 2558; addition to German Patent 467,930, 1922; *Chem. Abs.*, 1929, **23**, 1748; German Patent 541,910, 1928; *Chem. Abs.*, 1932, **26**, 2471; British Patent 309,875, 1927; *Chem. Abs.*, 1930, **24**, 718; all patents assigned to I. G. Farbenindustrie A.-G.

[81] I. G. Farbenindustrie A.-G., British Patent 324,538, 1929; *Chem. Abs.*, 1930, **24**, 3250. Also French Patent 682,056, 1929; *Chem. Abs.*, 1930, **24**, 4306; French Patent 683,587, 1929; *Chem. Abs.*, 1930, **24**, 4522. Beck and Diekmann, German Patent 556,732, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 310; I. G. Farbenindustrie A.-G., British Patent 352,512, 1930; *Brit. Chem. Abs.* **B**, 1931, 1039.

[82] I. G. Farbenindustrie A.-G., British Patent 312,405, 1928; *Chem. Abs.*, 1930, **24**, 984. *Cf.* Beck, Diekmann and Kremp, German Patent 552,986, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 5572.

[82a] Von Friedolsheim and Beller, German Patent 538,374, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 1766.

[83] Luther and Franzen, German Patent 492,755, 1927; *Chem. Abs.*, 1930, **24**, 2472; British Patent 315,813, 1928; *Chem. Abs.*, 1930, **24**, 1651; both patents assigned to I. G. Farbenindustrie A.-G.

[84] I. G. Farbenindustrie A.-G., British Patent 333,904, 1929; *Chem. Abs.*, 1931, **25**, 837.

[84a] I. G. Farbenindustrie A.-G., British Patent 386,552; *Chem. Abs.*, 1933, **27**, 2161.

A method of partially separating the acids was devised by Luther,[86] in which the crude acids are first neutralized with about one-third of the theoretical quantity of alkali. After separating the acids and soap solution, complete neutralization is effected. The first step removes the acids of low molecular weight, the high molecular weight acids being obtained in the second step.

Beck and Kremp[87] used concentrated acetic acid to effect a separation of acids and unsaponifiable material. After the oxidation of the paraffin wax, the crude product is treated at 60° C. with 95 per cent acetic acid, and the insoluble portion separated. The solution is allowed to cool, and the unsaponifiable material which separates is filtered off.

The same investigators suggested heating the crude oxidation products under pressure with ammonia, thus converting the acids to amides and ammonium salts.[88] The ammonium salts separate during the reaction and can be removed later. The amides are separated from the unchanged paraffins by extraction with petroleum ether. Both the amides and ammonium salts are then converted to the free acids by any convenient method.

James[88a] found isopropyl alcohol to be superior to methyl, ethyl or normal butyl alcohol in extracting the more highly oxidized portion (alcohols, esters, ethers, aldehydes and ketones) from the heavier fractions of oxidized oils. By employing an isopropyl alcohol-water mixture for the extraction of the fraction boiling above 200° C., two layers form. The top layer consists of a highly concentrated hydrocarbon portion and the lower layer, a mixture of the solvent and highly oxidized products. Another process employs liquid sulphur dioxide as an extraction solvent.[88b] The wax acids are thus dissolved, leaving the unsaturated hydrocarbons.

Distillation may be employed in effecting separation.[89] At a temperature of 150° to 300° C. and under a pressure of 10 to 50 mm., the product may be treated with a mist of finely divided inert liquid. One which boils below 105° C. is best. Water, benzene, tetrachlorethane, carbon tetrachloride, alcohol, toluene, or acetic acid together with inert gas carriers such as steam, carbon dioxide or nitrogen can be employed; or the crude material can be saponified to obtain an aqueous mixture consisting of magnesium, calcium and potassium soaps.[90] The soaps should be present in such proportions that the melting point of the crude product in the anhydrous condition is less than 150° C. The unsaponifiable matter can then be removed by distillation.

Low-boiling benzines have been employed by Hellthaler and Peter[91] to effect the separation of hydroxy acids from wax acids which do not contain hydroxyl groups. The process depends upon the solubility of the non-hydroxy wax acids in the benzines, as compared with the relative insolubility of the hydroxy acids. In a sample of oxidized paraffin wax, these investigators found 30 per cent of hydroxy acids.

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[85] I. G. Farbenindustrie A.-G., British Patent 321.399, 1928; *Chem. Abs.*, 1930, 24, 2909.

[86] German Patent 405,636, 1923; assigned to Badische Anilin- und Soda-Fabrik; *J.S.C.I.*, 1925, 44, 325B.

[87] German Patent 500,913, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, 24, 4792; U. S. Patent 1,880,677, Oct. 4, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 514.

[88] German Patent 522,055, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, 25, 3159.

[88a] U. S. Patent 1,835,600, Dec. 8, 1931.

[88b] Luther and Beller, German Patent 561,714, 1929; *Chem. Abs.*, 1933, 27, 990; British Patent 347,620, 1930; *Chem. Abs.*, 1932, 26, 2747; *cf.* British Patent 366,025, 1930; *Brit. Chem. Abs.* **B**, 1932, 332; all patents assigned to I. G. Farbenindustrie A.-G.

[89] Franzen and Kunze, German Patent 566,915, 1930; *Chem. Abs.*, 1933, 27, 2457; British Patent 358,278, 1930; *Chem. Abs.*, 1932, 26, 4973; French Patent 731,307, 1932; *Chem. Abs.*, 1933, 27, 734; all patents assigned to I. G. Farbenindustrie A.-G.

[90] I. G. Farbenindustrie A.-G., British Patent 380,707, 1932; *Brit. Chem. Abs.* **B**, 1932, 1040.

[91] U. S. Patent 1,885,199, Nov. 1, 1933; assigned to A. Riebeck'sche Montanwerke A.-G.; *Chem. Abs.*, 1933, 27, 1007.

According to Dovankov,[91a] however, the method of separation of hydroxy and non-hydroxy carboxylic acids by extraction with naphtha is impractical on a technical scale on account of the large amounts of solvent required. He reduced the amount of naphtha used to 3 to 5 times the weight of the acids by two methods. In one, concentrated sulphuric acid was added in small portions to a 3 to 1 solution of the acids. With each addition of sulphuric acid some hydroxy acids were precipitated. In the second, 0.3 to 0.8 per cent by weight of gaseous hydrochloric acid was introduced into a 5 to 1 naphtha solution of the wax acids, the separation of hydroxy acids being complete after 12 hours.

Varlamov[92] freed saponifiable matter from unsaponifiable in the following manner: the oxidation product is dissolved in benzine (boiling from 120° to 160° C.) and the calculated quantity of aqueous sodium hydroxide (1:5) is then added. The saponifiable portion was extracted leaving the unsaponifiable dissolved in the benzine.

Beck and Diekmann[92a] reduced the content of unsaponifiable material in wax acids by extraction with hydrocarbons which are themselves capable of being oxidized to fatty acids. The resulting mixture of hydrocarbon solvent and unsaponified constituents may then be oxidized to fatty acids. A sample of soap solution (saponified constituents) containing about 8 per cent of unsaponifiable substances was heated and passed countercurrent to the extracting hydrocarbons. The resulting soap solution contained 3 to 4 per cent of unsaponifiable substances.

The material obtained by oxidizing wax with nitric acid, or the oxides of nitrogen, may be refined by heating (under pressure) with dilute aqueous solutions of alkali or acid.[93] The volatile nitrogen compounds formed are removed by blowing with steam.

Mono- and dicarboxylic acids of high molecular weight can be separated from each other by treating oxidized wax with aliphatic hydrocarbons of low boiling point.[94] Organic solvents soluble in water can also be used. To such solvents is added enough water to effect solution of the dicarboxylic acids leaving the monoacids as insoluble residues.

Mention has been made of decolorizing the acids by pressing at high pressure and low temperatures. Other methods for bleaching and deodorizing such acids include both oxidation and reduction. Thus, the crude acids may be oxidized with nitric acid,[94a] chromic acid, potassium permanganate or hydrogen peroxide at temperatures around 105° C., or in an electrolytic cell containing oxygen-transferring agents, such as chromic or ferric sulphate;[95] or the mixture of acids may be treated with a metal and an acid which react to liberate hydrogen, as for example, zinc and sulphuric acid.[96] Active carbon has also been used for decolorizing.[96a]

[91a] *Masloboino-Zhirovoe Delo,* 1932, No. 1, 54; *Chem. Abs.,* 1932, **26**, 4704.

[92] *Masloboino-Zhirovoe Delo,* 1932, No. 7, 39; *Chem. Abs.,* 1933, **27**, 3595.

[92a] U. S. Patent 1,920,344, Aug. 1, 1933; *Chem. Abs.,* 1933, **27**, 4817; British Patent 368,869, 1930; *Chem. Abs.,* 1933, **27**, 2162; French Patent 717,674, 1931; *Chem. Abs.,* 1932, **26**, 2883; all patents assigned to I. G. Farbenindustrie A.-G.

[93] Beck, Diekmann and Kremp, German Patent 566,450, 1930; *Chem. Abs.,* 1933, **27**, 1007; U. S. Patent 1,912,123, May 30, 1933; *Chem. Abs.,* 1933, **27**, 3948; British Patent 364,574, 1930; *Brit. Chem. Abs.* **B**, 1932, 313; all patents assigned to I. G. Farbenindustrie A.-G.

[94] I. G. Farbenindustrie A.-G., French Patent 721,796, 1931; *Chem. Abs.,* 1932, **26**, 4066.

[94a] Beck and Diekmann, German Patent 568,130, 1931; *Chem. Abs.,* 1933, **27**, 1894; addition to German Patent 528,361, 1927; *Chem. Abs.,* 1931, **25**, 4728; both patents assigned to I. G. Farbenindustrie A.-G.

[95] Pungs, German Patent 528,361, 1927; *Chem. Abs.,* 1931, **25**, 4728; U. S. Patent 1,871,082, Aug. 9, 1932; *Chem. Abs.,* 1932, **26**, 5576; British Patent 299,149, 1927; *Chem. Abs.,* 1929, **23**, 3118; all patents assigned to I. G. Farbenindustrie A.-G.

MECHANISM OF THE OXIDATION OF PARAFFIN

The influence of the elements of the oxygen group on paraffin wax was investigated by Siebeneck,[97] whose findings correspond somewhat to those of other investigators. The wax can be oxidized when heated to 135° C. by either air or oxygen, the rate of oxidation being somewhat slower with air. At the end of 10 hours, acid vapors are evolved, and at the end of 22 hours a product was obtained which contained 30 to 40 per cent of saponifiable material. Longer oxidation increased the quantity of saponifiable material in the product. The acids produced were saturated aliphatic acids and the volatile product consisted of acids of lower molecular weight of the same series together with some water. The volatile material corresponded to about 7 per cent of the paraffin used.

With hard paraffin and sulphur the reaction appears to be a dehydrogenation, as hydrogen sulphide is obtained in large quantities together with carbon disulphide. After heating for 72 hours at 230° C., a fat-like, black mass was obtained. On extraction with carbon disulphide followed by ether, a black amorphous substance was obtained, whose composition corresponded closely to the formula $(C_8S)_x$. This substance was rather indifferent towards alkalies and organic solvents, but was attacked by concentrated sulphuric or nitric acid. Reaction between the paraffin and sulphur takes place at slightly higher temperatures than with air or oxygen, the reaction starting at 150° C. and proceeding rather rapidly at 230° C.

Selenium and tellurium react similarly but require higher temperatures (300° to 700° C.). No selenium or tellurium compounds analogous to the sulphur compound were obtained. Small quantities of either sulphur or selenium seem to inhibit the action of oxygen on paraffin.[98]

In another study, brown-coal paraffin, melting at 54° C., was oxidized for 55 hours at 135° C., and analyses were made at various time intervals.[99] During the first 10 hours there was a rapid absorption of oxygen accompanied by the formation of formic acid and other low molecular weight acids. Ester formation, according to Siebeneck, appeared to be the primary reaction, the acids resulting from the decomposition of the ester. The second stage in the oxidation was reached in about 12 hours when the evolution of carbon dioxide began. During the second stage the ester value and saponification value both increased while the acid value more than doubled. The third stage occurred after 33 hours, during which the ester value decreased, the saponification value remained about constant, and the acid value increased. The products formed in the second stage, between 12 and 33 hours, are the ones which are most likely to find commercial use. They are waxy, of a light color, and can be recovered by steam distillation.

At a slightly higher temperature (183° to 184° C.) Kailan and Olbrich[100] found that oxidation of paraffin wax proceeded more rapidly in the second period of 25 hours than during the first period of the same length. The quantity of carbon dioxide evolved was proportional to the time of the reaction, and the quantity of saponifiable matter increased from 1.46 per cent at the end of 25 hours to 8.04 per cent at the end of 100 hours.

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[96] Franzen and Luther, U. S. Patent 1,757,455, May 6, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1930, 24, 3355.

[96a] Beck, Diekmann and Kremp, German Patent 552,986, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 5572.

[97] *Petroleum Z.*, 1922, 18, 281; *Chem. Abs.*, 1922, 16, 3200.

[98] *Cf.* effect of sulphur on the autoxidation of petroleum distillates, Chapter 40.

[99] Siebeneck, *Petroleum Z.*, 1922, 18, 1193; *Chem. Abs.*, 1923, 17, 466.

[100] *Monatsh.*, 1927, 48, 537; *Chem. Abs.*, 1928, 22, 213.

This latent period has also been observed by other workers. The time required for a paraffin wax to reach a given oxygen content (7 per cent) was determined by Francis and his collaborators, who obtained the following values.[101] For wax at 100° C., oxidized with oxygen, the time required was 1060 hours. With air at the same temperature the time was too long to be determined, but at 120° C. it required 285 hours. With wax containing 5 per cent turpentine, the time required with air at 100° C. was 800 hours, and with oxygen, 320 hours. When the temperature was increased to 135° C., the time required with air was 285 hours, but with oxygen only 46 hours were necessary. On the other hand, wax from lignite, which contained 0.7 per cent oxygen, reached a 7 per cent oxygen content after 24 hours at 135° C.

It was further observed that the latent period could be reduced by (1) heating the wax[102] before oxidation in a vacuum, (2) employing catalysts, and (3) pretreating with sulphuric acid at 100° C. Heating the wax in a vacuum did not alter its physical constants, but it did slightly increase its solubility in chloroform or acetone. When this heated wax was recrystallized from acetone it again showed the same latent period as the untreated wax, the acetone evidently extracting a substance which catalyzed the oxidation. The latent period may therefore be ascribed to (1) formation of a positive catalyst, (2) destruction of a negative catalyst present in the original material, or (3) isomeric changes brought about by the action of heat, particularly the formation of unsaturated compounds.

In investigating the composition of paraffin wax, Francis[103] found that oxidation did not take place on passing a rapid current of air for 280 hours at 110° C., nor by oxygen in 700 hours at 100° C. With oxygen at the end of 1276 hours at 100° C., a product containing 74.7 per cent carbon, 11.6 per cent hydrogen, and 13.7 per cent oxygen was obtained. Above 130° C., however, paraffin could be easily oxidized with air. In the presence of a small quantity of turpentine a selective oxidation takes place at 100° or 110° C. and apparently only one class of constituents is attacked. The resulting products are therefore less numerous than those obtained at higher temperatures and are close in molecular weight to the hydrocarbons which occur in the wax. The part played by the turpentine is not well understood.

Since two synthetic normal hydrocarbons, n-hexadecane ($C_{16}H_{34}$) and n-dotriacontane ($C_{32}H_{66}$), were not oxidized in the presence of small quantities of turpentine, it would appear that there were some constituents of wax other than normal aliphatic hydrocarbons which were oxidized. This view was further strengthened by the fact that when paraffin wax was distilled in a high vacuum it was possible to obtain certain fractions which were more easily oxidized than others.

In addition to the volatile reaction products obtained in the above oxidations, the substances remaining in the reaction vessel consisted of unattacked hydrocarbon, non-acid oxidized materials, and some acids of high molecular weights. The acidic substances were divided into four groups, α, β, γ, and δ. The α- and β-acids, which amounted to 32 per cent of the total, are the principal products of air oxidation. The α-acids are insoluble in water or aqueous alcohol, and possess low melting points and high molecular weights. The β-acids possess higher melting points and lower molecular weights. The γ-acids are liquids which are slightly soluble in aqueous alcohol. The δ-acids are rather soluble in water. Oxidation with pure oxygen yields principally β- and γ-acids.

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[101] Francis, Millard, Rutt, Watkins, Wallington, and Garner, *J.C.S.*, 1924, **125**, 381.

[102] *Cf.* Kelber, *Ber.*, 1920, **53**, 66, 1567.

[103] Francis, Pope, Coysh, and Gauntlett, *J.C.S.*, 1922, **121**, 496; *J.C.S.*, 1926, **128**, 2377; Gutt and Plotko (*Azer. Neft. Khoz.*, 1930, No. 9, 108; *Brit. Chem. Abs.* B, 1931, 284) found 150° C. to be the optimum temperature for air oxidation.

The non-acid products consisted of secondary alcohols and ketones and probably some dihydric alcohols, hydroxyketones and diketones. These non-acid products also decrease in quantity as oxidation proceeds, as they are converted to acids. The ketones and secondary alcohols had chains of 26 to 29 carbon atoms. The secondary alcohols are first formed and these are then oxidized to the ketones. As shown by x-ray examination of the ketones, the point at which the carbon chain is attacked seems to be the third or fourth carbon atom from the end.

Later, however, it was found that triacontane ($C_{30}H_{62}$) could be oxidized at 95° C. by air in the presence of turpentine and that the nature of the products and the velocity of reaction were both similar to that of paraffin wax.[104] The acid products isolated were succinic acid; cerotic acid, $C_{26}H_{52}O_2$, which was identical with that prepared from beeswax; a small amount of the acid, $C_{24}H_{48}O_2$, which was identical with that formed by oxidizing paraffin; and three acids of the following formulas, $C_{16}H_{32}O_2$, $C_{20}H_{40}O_2$, and $C_{22}H_{44}O_2$. The inert products included a ketonic alcohol or dihydroxy-compound of the formula $C_{30}H_{60}O_2$, and a ketone $C_{30}H_{60}O$. The point of attack was again indicated to be the third or fourth carbon atom from the end of the chain.

The failure to oxidize triacontane in the first instance was traced to impurities, particularly iodine which was not removed completely in the synthesis of the substance. These greatly prolonged the period of time during which no oxidation occurred. Later this same compound, triacontane, was synthesized by the electrolysis of sodium palmitate, and the product so obtained was not contaminated with halogens which inhibit oxidation.

In Chapter 37 the work of Landa on the oxidation of paraffin wax was mentioned. His results led to the conclusion that slow oxidation of the homologues of methane took place according to Bone's hydroxylation theory and that the presence of alcohols and ketones among the oxidation products indicated the presence of branched-chain hydrocarbons in paraffin wax. His further work on the oxidation of triacontane, which is a straight-chain compound, appeared to substantiate this.[105] This product was made both from Japanese wax and by the electrolysis of an alcoholic solution of potassium palmitate. The oxidation products included aliphatic acids (formic, butyric and valeric), aldehydes (hex- and hept-aldehydes) from which acids were formed, and a small amount of unsaturated hydrocarbons and carbon monoxide and dioxide, but no alcohols or ketones. The oxidation of this substance was carried out at 290° to 310° C. and no preferential catalyst (such as turpentine) was used. Both of these factors, no doubt, explain why he obtained products of lower molecular weight than did Francis and Wood.

Landa has also suggested that slow oxidation, or gradual combustion of petroleum oils may be used as a test for the presence of paraffin. Oils containing paraffin give a positive aldehyde test with Schiff reagent after oxidation.

In attempting to get a clearer insight into the nature of the reactions taking place during the oxidation of paraffins, Salway and Williams[106] studied the oxidation of two pure compounds, hexadecane and stearic acid. The former was chosen as representative of paraffin hydrocarbons. Since the higher acids produced by oxidation of paraffin hydrocarbons subsequently undergo further change as the action is continued, stearic acid was chosen to represent an oxidation product. The oxidation was carried out for 24 hours at 120° to 130° C. in a current of oxygen with 2 per cent of manganese stearate as a catalyst.

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[104] Francis and Wood, *J.C.S.*, 1927, 1897.

[105] Landa, *Paliva a topeni*, 1929, 11, 1; *Chem. Abs.*, 1929, 23, 4667. See also *Compt. rend.*, 1928, 187, 948; *Chem. Abs.*, 1929, 23, 1866; *Chem. Listy*, 1928, 22, 294, 499; *Brit. Chem. Abs.* **B**, 1929, 88.

[106] *J.C.S.*, 1922, 121, 1343; *Chem. Abs.*, 1922, 16, 3064.

From the hexadecane were obtained 4 per cent of volatile acids, carbon dioxide, formic and acetic acids. The rest of the reaction product consisted of about 70 per cent acidic substances and 30 per cent unchanged hexadecane. The acidic substances, after extracting with sodium hydroxide, consisted of a pale yellow oil, about 20 per cent of which was volatile with steam, and appeared to be principally hexanoic and nonanoic acids. The non-volatile portion was largely lactonic acids similar to those produced by the oxidation of stearic acid.

These investigators found that the oxidation of stearic acid yielded about 5 per cent of volatile acids, principally carbon dioxide and formic acid together with some acetic and higher acids and about 8 per cent of water-soluble acids, of which about 35 per cent were volatile with steam and proved to be formic, acetic, and butyric, and the remainder, dibasic acids of the malonic acid series. The main product of the reaction, however, consisted of hydroxy-acids and their lactones, none of which could be isolated in a pure condition.

The results obtained by Salway and Williams are in agreement with the earlier findings of Zerner.[107] The latter oxidized stearic acid under practically the same conditions. In addition to the volatile acids, he also obtained an alcohol of the formula $C_{12}H_{20}O$. Among the dibasic acids formed, succinic and pimelic were identified. The main product, however, was a mixture of hydroxy-acids which formed soaps that lathered well in water but could not be salted out. The results of the oxidation of ethyl stearate under the same conditions did not seem to indicate, because of the disappearance of the ethoxy-group, that stearic acid was preferentially oxidized at either end of the carbon chain. Compounds containing eight or less carbon atoms were not oxidized under the same conditions.

Pflugk[107a] investigated the influence of various factors upon the oxidation of paraffins to acids. The optimum temperature for air oxidation was 160° C. Lengthy incubation periods were observed at lower temperatures. The yield of fatty acids increased to a limit with increase in air-current velocity, the most favorable rate being 1100 to 1300 liters per hour per 300 grams of paraffin. A small moisture content (1.2 per cent by volume) increased the yield slightly. According to Pflugk, the mechanism of formation of fatty acids is as follows: Unsaturated compounds are formed by elimination of 2 hydrogen atoms as hydrogen peroxide. Fracture of the chain and anhydride or acid formation then takes place. Peracids and peroxides were found in the products, which was accounted for by reaction of hydrogen peroxide with the wax acids or anhydrides. Acid substances, when present, acted as catalysts but alkalies did not.

SUMMARY

The paraffin waxes from petroleum or similar products can be oxidized to organic acids. The acids thus produced may be roughly divided into two classes: (1) volatile acids of the type of acetic acid, and (2) water insoluble acids which contain ten or more carbon atoms. The term "wax acids" has been used to describe these water-insoluble acids. A large proportion of these acids often contain an uneven number of carbon atoms in the molecule, in contradistinction to the typical "fatty acids" which contain an even number of carbon atoms. Francis[108] and his co-workers have pointed out the difficulty of identifying the acids obtained by the oxidation of paraffin wax or of the alcohols from Chinese and carnauba wax. It arises from the fact that the mixed crystals of acids of two different carbon contents show properties corresponding to those of pure compounds of higher carbon content. The products from the oxidation of natural compounds, purified by the customary procedures, may therefore really be mixtures. These wax acids, however, can be used in the production of soaps, and also, no doubt, in the production of synthetic fats.

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[107] *Naturprodukte*, 1923, 83; *Chem. Abs.*, 1924, 18, 1112.

[107a] *Braunkohlenarch.*, 1932, No. 37, 1; *Chem. Zentr.*, 1932, 2, 3959; *Brit. Chem. Abs.* **B**, 1933, 819; *Chem. Abs.*, 1933, 27, 2423.

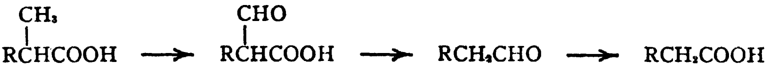
For producing wax acids on a commercial scale, air appears to be the best and cheapest oxidizing agent. Other oxidizing agents (pure oxygen, ozone, oxides of nitrogen) as well as electrochemical methods can be used. The optimum temperature for oxidation is about 150° to 180° C. At higher temperatures, more vigorous oxidation takes place, and a higher percentage of lower molecular weight products are obtained. At lower temperatures, the time required for oxidation is excessive. Oxidizing under increased pressures, at least in some instances, aids in speeding up the reaction.

The oxidation is preceded by a latent period during which oxygen is absorbed with the formation of only a small quantity of acids. This period may be shortened by the use of catalysts, particularly organic acids such as stearic or cinnamic or their salts. Turpentine has been mentioned as a catalyst for the selective oxidation of certain constituents of paraffins. The use of alkalies as catalysts appears to be questionable.

Other products in addition to acids and alcohols are aldehydes and ketones. It seems to be a general rule that aldehydes are the principal products if the hydrocarbon consists for the most part of straight-chain compounds. Alcohols and ketones are more likely to be obtained from the branched-chain hydrocarbons. In some instances, the presence of hydroxy-acids, lactones, and even diketones, has been reported.

Three general theories have been suggested for the mechanism of the oxidation of paraffin: (1) that oxidation proceeds according to the hydroxylation theory; (2) that the hydrocarbons during heating lose hydrogen and become unsaturated, and oxidation then takes place at the double bond accompanied by a breaking up of the molecule; and (3) that the formation of esters takes place first, followed by the oxidation of these substances to acids.

For any α-substituted acids that might be present or formed, the oxidation mechanism suggested by Raper[109] may be applicable. This mechanism is based on Knoop's rule of β-oxidation, which states that the carbon atom of the methyl group present in such acids in the β-position to the carboxyl group, is oxidized in preference to the β-carbon atom in the main chain, thus:



$$\underset{\text{R}\overset{|}{\text{C}}\text{HCOOH}}{\text{CH}_3} \longrightarrow \underset{\text{R}\overset{|}{\text{C}}\text{HCOOH}}{\text{CHO}} \longrightarrow \text{RCH}_2\text{CHO} \longrightarrow \text{RCH}_2\text{COOH}$$

The whole problem of the oxidation of paraffins is a complicated one. Apparently contradictory results have been reported, probably because of the lack of definite methods of determining the composition of the various components of different oxidized waxes.[110] When improved methods become available, many of the apparent discrepancies in the results of various workers will no doubt disappear.

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[108] Francis, Piper and Malkin, *Proc. Roy. Soc. (London)*, 1930, **128A**, 214; *Chem. Abs.*, 1930, **24**, 5019.

[109] *Biochem. J.*, 1914, **8**, 320; *Chem. Abs.*, 1914, **8**, 3781.

[110] For the composition and crystal forms of petroleum wax see Ferris, Cowles and Henderson, *Ind. Eng. Chem.*, 1931, **23**, 681. For x-ray diffraction study of fractioned waxes see Clark and Smith, *Ind. Eng. Chem.*, 1931, **23**, 697.

Chapter 44

Oxidation from the Standpoint of Detonation

GASEOUS EXPLOSIONS. LIMITS OF INFLAMMABILITY

For each pair of gases forming a combustible mixture there is both an upper and a lower limit of inflammability. The lower limit corresponds with the minimum quantity and the higher, or upper, limit with the maximum quantity of combustible gas capable of conferring inflammability on the mixture. For example, at ordinary pressures and temperatures the limiting concentrations of methane-air mixtures are approximately 5 and 14 per cent methane.[1]

One factor which affects the limits of inflammability is the direction of the propagation of the flame. Generally these limits are slightly wider for upward propagation than for downward or for horizontal propagation. Other factors which influence the limits of inflammability are the diameter and length of the vessel, and whether it is open or closed. Over small ranges, variations in temperature or pressure do not appear to have much effect on the limits. Over great increases of temperature, however, there is generally a widening in the limits. Pressure decreases are usually accompanied by a narrowing of the limits. This may not be perceptible for a decrease of a hundred millimeters or so in pressure, but as the pressure is further diminished, the upper and lower limits begin to approach one another and finally coincide. An increase in pressure is not invariably accompanied by a widening of the limits. In many instances, a narrowing of the limits of inflammability is brought about by this change. Turbulence also appears to be specific in its effect. For example, the lower limits of inflammability of both methane and ethane in air are lowered by turbulence, although the range of inflammability of ether-air mixtures is widened.

The figures in Table 144 give the limits of inflammability in air of some of the more common gases or vapors. These limits were obtained in tubes of about the same diameter (7.5 centimeters) and with upward propagation of the flame.[2]

TABLE 144.—*Limits of Inflammability in Air (Upward Propagation of Flame).*

Gas or Vapor	Gas Per Cent	Gas or Vapor	Gas Per Cent
Hydrogen	4.15–75.0	Ethylene	3.0–34.0
Carbon Monoxide	12.8 –75.0	Propylene	2.2– 9.7
Methane	5.35–14.9	Butylene	1.7– 9.0
Ethane	3.12–15.0	Acetylene	2.6–80.5
n-Pentane	1.42– 8.0	Benzene	1.4– 7.5
		Toluene	1.3– 6.8

The variations in the limits of inflammability with the direction of the propagation of flame for acetylene in air are as follows:

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[1] See Coward and Jones, Limits of Inflammability of Gases and Vapors, *U. S. Bur. Mines Bull.* 279. 1928. This is an excellent summary of this subject and gives the limits for a large number of gases and vapors. An extensive bibliography is included.

[2] White, *J.C.S.*, 1922, 121, 1244; *ibid.*, 1924, 125, 2387.

2.60–80.5	Upwards
2.68–78.5	Horizontal
2.78–71.0	Downwards

The upper and lower limits of inflammability for flame propagation upwards, horizontally, and downwards have been determined by White[3] for mixtures of air with hydrogen, hydrogen sulphide, carbon monoxide, and various saturated and unsaturated hydrocarbons containing up to five carbon atoms. In making these determinations closed tubes of various diameters were used. It was observed that, with tubes of 7.5 centimeters diameter, wall-cooling exerted very little influence on the values of the lower limits, but the results for the upper limits occasionally differed appreciably from those obtained with a 5-centimeter tube, probably because of convection. In many instances, the lower limits of the mixtures could be calculated with a reasonable degree of accuracy from the calorific value of the gas. With several mixtures it was possible to obtain similarly a rough approximation of the upper limits. The type of bond which must be ruptured or broken when the gas or vapor is burned seemed to greatly influence these values.

This work was extended[4] to include gaseous mixtures, such as methane and hydrogen, ethylene and hydrogen, and others. The results show that a fair approximation to the limiting values of the mixtures can be secured by the application of the law developed by Le Chatelier,[5] which states that a mixture of any two limit mixtures (both upper or both lower) will itself be a limit mixture. These approximations were usually closer to the experimental values for the lower rather than for the upper limits, and for downward rather than upward flame propagation. For both gas and vapor mixtures the type of flame started often determined whether or not propagation would occur.

White[6] also showed the effect of temperature on the upper and lower limits for downward propagation of the flame. In all instances the limits were widened, and the degree, or percentage change in the limits, differed with the various gases studied.

The upper and lower explosive limits of more complicated gas mixtures, such as those encountered in the manufacture of city gas, have been determined by Yeaw.[7] A small quantity of illuminating constituents was found to reduce the upper limits from about 70 per cent of the gas to 30 per cent, but the lower limit was affected to a much smaller degree. The upper limit was unaffected by large changes in the ratio of hydrogen to carbon monoxide, as they both have ap-

TABLE 145.—*Analysis and Explosive Limits of Various Gas Mixtures.*

								Limits (Gas in Air)	
Gas	CO_2	Illuminants	O_2	CO	H_2	CH_4	N_2	Lower	Upper
	Per Cent								
Oven	1.9	3.9	0.4	6.3	54.4	31.5	1.6	5.0	28.4
Coal	2.4	2.7	0.4	9.7	44.9	28.9	11.0	5.6	30.8
Mixed	2.5	3.2	0.5	10.5	47.0	25.8	10.5	5.6	31.7
Carbureted blue	4.6	7.3	0.3	36.0	37.0	9.6	5.2	6.4	37.7
Blue	6.2	0.0	0.3	39.2	49.0	2.3	3.0	6.9	69.5
Producer	6.2	0.0	0.0	27.3	12.4	0.7	53.4	20.7	73.7

[3] White, *J.C.S.*, 1924, 125, 2387.
[4] White, *J.C.S.*, 1925, 127, 48.
[5] *Ann. mines*, 1891, (8) 19, 388; see Coward and Jones, *op. cit.*
[6] *J.C.S.*, 1925, 127, 672.
[7] *Ind. Eng. Chem.*, 1929, 21, 1030. For the inflammable limits of exhaust gases from automobiles see Jones, *Ind. Eng. Chem.*, 1928, 20, 901.

proximately the same upper limits. The upper limit of the gas mixture was lowered by increasing the methane content. These changes are illustrated by the data in Table 146.

The upper or lower explosive limit (L) of a gas mixture can be calculated by the use of the formula[8]

$$L = \frac{100}{\frac{a}{A} + \frac{b}{B} + \frac{c}{C} + \ldots}$$

in which a, b, and c are the relative proportions of the components of the mixture (in parts per hundred of the mixture) and A, B, and C are their respective inflammability limits. In applying this formula to such complicated mixtures as those just mentioned above, it is better to follow a modification suggested by Jones.[9] This is illustrated by taking the analysis of the producer gas given in the preceding data, and grouping together the carbon dioxide and monoxide, and the nitrogen and hydrogen.

Mixtures	Total	Ratio of Inert Gas to Combustible Gas	Limits of Inflammability[a] Lower	Upper
	Per Cent		——Per Cent——	
(1) 27.3% CO 6.2% CO_2....	33.5	0.2	17.0	70.0
(2) 12.4% H_2 53.4% N_2.....	65.8	4.3	23.0	76.0
(3) 0.7 CH_4	0.7	0.0	5.5	14.5

[a] For these values and methods of obtaining them see Jones, *Ind. Eng. Chem.*, 1928, **20**, 901.

Substituting these values in the formula,

$$\text{Lower Limit} = \frac{100}{\frac{33.5}{17.0} + \frac{65.8}{23.0} + \frac{0.7}{5.5}} = 20.2\%$$

$$\text{Upper Limit} = \frac{100}{\frac{33.5}{70.0} + \frac{65.8}{76.0} + \frac{0.7}{14.5}} = 71.8\%$$

For gases containing illuminants, the limits of inflammability of the illuminants, for the purposes of calculation, may be taken as 2 and 8 per cent, respectively. The calculated values in most instances are in good agreement with the observed values, but generally slightly lower.

It has been pointed out by Jones and Perrott[10] that, although the explosive limits of hydrocarbon vapors from petroleum and its products when mixed with air range from about 1 per cent (lower limit) to 12.5 per cent (upper limit), such mixtures can be made non-explosive by the addition of sufficient inert gases such as nitrogen, carbon dioxide, or flue gas. Jorissen and Meuwissen[11] showed that explosions of methane-air mixtures can be inhibited by the addition of non-inflammable vapors of organic liquids such as carbon tetrachloride or trichloroethylene. Crouch and Carver[12] found that methyl alcohol-air and acetone-air mixtures are rendered non-explosive when nitrogen is added to the mixtures in proportions sufficient to reduce the oxygen content to less than 11 per cent.

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[8] This formula was derived by Coward, Carpenter, and Payman (*J.C.S.*, 1919, **115**, 27) and its derivation was based upon the theoretical considerations of Le Chatelier (*Ann. mines*, 1891, (8) **19**, 388).

[9] *Loc. cit.*

[10] *Quart. Natl. Fire Protect. Ass.*, 1930, **23**, 385; *Chem. Abs.*, 1930, **24**, 6018.

[11] *Rec. trav. chim.*, 1924, **43**, 591; *Chem. Soc. Abs.*, 1925, **128** (2), 53.

[12] *Ind. Eng. Chem.*, 1925, **17**, 641.

These investigators also observed that Le Chatelier's law held for the mixtures studied.

Jorissen[13] called attention to the fact that a vapor added to a hydrocarbon-air mixture may act either as a positive or a negative catalyst. For example, 1.75 per cent of isobutyl chloride vapor added to a 10 per cent methane-air mixture renders it non-inflammable, but a non-inflammable 2.2 per cent methane-air mixture is rendered inflammable by this same proportion of isobutyl chloride. Propyl bromide, silicon tetrachloride, and sulphuryl chloride behave in a similar manner.

Ignition of Gases by Heated Surfaces

Mason and Wheeler[14] mentioned that the exposure of inflammable mixtures to heated surfaces was one of the earliest methods of determining ignition temperatures.[15] Determinations by this method, as usually made, however, do not give absolute values since the results are affected by the nature and the extent of the solid igniting surface. By modifying the usual method, Mason and Wheeler were able to obtain what they called the relative ignition temperature and also the composition of the most readily ignited mixture of methane and air. Briefly, they introduced known mixtures of methane and oxygen into a small quartz cylinder (81 cc. capacity) which had been heated to a predetermined temperature. The temperature to which it was necessary to heat the walls of the bulb in order that a given mixture would ignite was taken as the ignition temperature. Table 146 gives some of the data which were obtained:

Table 146.—*Relative Ignition Temperatures of Methane-Air Mixtures.*

Methane in Air Per Cent	Relative Ignition Temperature ° C.	Methane in Air Per Cent	Relative Ignition Temperature ° C.
2.00	711	8.00	701
3.00	700	8.80	707
3.95	696	10.00	714
5.85	695	11.75	724
7.00	697	14.35	742

The "pre-flame period" or "lag on ignition" was defined as the time interval between the introduction of the gas into the hot cylinder and the appearance of the flame. For methane-air mixtures containing between 2.5 and 13.0 per cent methane the lag varied from 10 to 15 seconds when the vessel was just at the relative ignition temperature. This period decreased with decreasing concentrations of methane and as the temperature of the cylinder was increased beyond the relative ignition temperature. It was also noted that ignition was accompanied by a sudden rise of pressure within the quartz vessel.

Continuing their work on ignition temperatures, Mason and Wheeler[16] determined these values for various mixtures of paraffins and air. Their data, some of which are given in Table 147, showed, however, that the relative ignition temperatures for hydrocarbon-air mixtures of approximately the same concentration decreased as the molecular weight of the hydrocarbon increased.

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[13] *Coll. Czech. Chem. Comm.*, 1930, **2**, 288; *Brit. Chem. Abs.* **A**, 1930, 1002.

[14] *J.C.S.*, 1922, 121, 2079.

[15] The combustion of hydrocarbons principally in air is discussed in this chapter. For the combustion of carbon monoxide-air mixtures see Fenning, *Phil. Trans.*, 1926, **225A**, 331; *Brit. Chem. Abs.* **B**, 1926, 258. For the combustion of hydrogen-air and carbon monoxide mixtures, see Bone and Haward, *Proc. Roy. Soc.*, 1921, **100A**, 67; *J.S.C.I.*, 1921, **40**, 802A; and Bone, Townend and Scott, *Proc. Roy. Soc.*, 1928, **120A**, 546; *Brit. Chem. Abs.* **A**, 1928, 1193. For the influence of nitrogen tetroxide on the combustion of hydrogen and oxygen see Thompson and Hinshelwood, *Proc. Roy. Soc.* (*London*), 1929, **124A**, 219; *Brit. Chem. Abs.* **A**, 1929, 657. For the burning of hydrocarbons in nitrous oxide, see Dixon and Higgins, *Fuel*, 1927, **6**, 232; *Brit. Chem. Abs.* **B**, 1927, 513.

[16] *J.C.S.*, 1924, **125**, 1869.

TABLE 147.—*Relative Ignition Temperatures of Hydrocarbons in Air.*

Hydrocarbon in Air	Relative Ignition Temperature ° C.
2.45% Methane	690
2.80% Ethane	571
2.50% Propane	552
2.60% Butane	531
2.75% Pentane	520

The duration of the lags on ignition for all mixtures of methane and air when oxygen was in excess was between 10 and 16 seconds. As the methane concentration was increased, the lag decreased, being about 6.6 seconds (at 720° C.) for a 12.8 per cent methane mixture. With ethane the reverse appeared to take place, as the lag was 28 seconds for a 1.9 per cent ethane mixture at 594° C. and 144 seconds for 10.6 per cent ethane at 534° C. Propane and butane behaved similarly to ethane. The lags for the former varied from 20 to 56 seconds and for the latter from 22 to 25 seconds. Pentane, on the other hand, resembled methane. The lags for the mixtures containing 1.5 to 3.75 per cent pentane were about 15 seconds, and for a 7.65 per cent mixture, about 5 seconds.

These pre-flame periods or lags on ignition, however, are a measure of the relative ignitibility when the gaseous mixtures were introduced into the quartz cylinder heated to a temperature well above the relative ignition temperature. With a temperature, for example, of 600° C., the lag decreased with increasing concentration of hydrocarbon, and with increasing molecular weight. This was true for all the hydrocarbons except methane, the relative ignition temperature of which is well above 600° C.

When mixtures of methane and oxygen, which in turn were mixed with an inert gas, were admitted to a quartz reaction vessel, those reactions which resulted in the production of a flame were thermal reactions catalyzed by the products of an initial slow and flameless combustion.[17] The total amount of heat acquired by the reacting gases depended upon the thermal properties of the inert gas, which absorbs a portion of the heat developed by the oxidation processes. For example, when the nitrogen in methane-air mixtures was replaced by argon, which has both a lower specific heat and lower thermal conductivity, the ignition temperatures of the mixtures were decreased. Replacement of the nitrogen by helium, a gas of high thermal capacity, on the other hand, raised the ignition temperatures. Among the oxidation products formed during the lag on ignition were formaldehyde and carbon monoxide.[18] Addition of either one of these products (about 0.02 per cent) to a methane-air mixture lowered its ignition temperature and shortened the period of lag. Formaldehyde was more effective than carbon monoxide, however. Other substances, such as ethyl iodide or bromide, carbon tetrachloride, traces of iodine, and lead tetraethyl, raised the ignition temperatures of methane-air mixtures and also decreased the speed of the reactions which occur below the ignition temperatures. The inhibiting action of these substances appeared to take place on the surfaces of the reaction vessel.

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[17] Naylor and Wheeler, *J.C.S.*, 1931, 2456.

[18] Among the intermediate products of the combustion of methane and oxygen which have been identified are formaldehyde, hydrogen peroxide, and ozone. (Riesenfeld and Gurian, *Z. phys. Chem.*, 1928, 139, 169; *Brit. Chem. Abs.* **A**, 1929, 289.) In the combustion of methane in oxygen the yield of ozone increases as the quantity of excess oxygen increases, although the yields of hydrogen peroxide and formaldehyde decrease. When oxygen burns in methane the yield of hydrogen peroxide again decreases but that of formaldehyde increases as the quantity of excess methane increases. No ozone is formed. The mechanism of the formation of these products was considered to involve the decomposition of the methane into methylene (CH_2) and atomic hydrogen. The atomic hydrogen forms mainly molecular hydrogen and some hydrogen peroxide. The methylene burns partly to carbon monoxide and formaldehyde. Further oxidation of these products gives water and carbon dioxide.

Lewis[19] showed that for paraffin hydrocarbon-air mixtures there is a critical temperature at which chemical reaction takes place readily with an increase in the number of molecules. This was demonstrated by slowly heating a given quantity of the liquid hydrocarbon in a large cylindrical bulb while the pressure on the bulb was slowly increased so as to keep the gas volume constant. If no chemical change took place the temperature-pressure curves should follow approximately the gas laws. In the case of the hydrocarbon-air mixtures a sudden rise in pressure, or inflexion, was always noted, thus indicating chemical reaction. The temperature at which this rise occurred was called the critical inflexion temperature (C. I. T.) and was dependent upon the molecular weight of the hydrocarbon. For example, the critical inflexion temperatures of some paraffins are as follows: pentane, 253° C.; hexane, 232° C.; heptane, 212° C.; octane, 198° C. These values were slightly lower for the normal hydrocarbons than for the isohydrocarbons. Thus the critical inflexion temperature of n-pentane is 253° C. but that of isopentane is 259° to 260° C. These values were only slightly affected by the concentration of the hydrocarbon vapor in the apparatus. Once the inflexion temperature was passed the gas mixtures then appeared to be stable up to about 450° C.

In considering the mechanism of the oxidation it appeared that the first step was a primary dehydrogenation, followed by oxidation of the hydrogen to water. This would account for (1) an increase in the number of molecules at the critical inflexion temperature, (2) the presence of water among the products of oxidation, and (3) the formation of unsaturated hydrocarbons at temperatures near the critical inflexion temperature.

Metallic catalysts were divided by Lewis into two classes: (1) promoters of detonation and (2) "antiknocks." To the former class belong such catalysts as platinum which promotes the reaction $2H_2 + O_2 \rightarrow 2H_2O$. To the latter belongs lead tetraethyl which actually retards either this reaction or the action of oxygen on the hydrocarbons. Unsaturated compounds are effective as antiknocks since they have a smaller hydrogen content, hence, are less likely to be dehydrogenated and because they have a tendency to combine with the hydrogen evolved from the saturated hydrocarbons. The latter explanation may also account for the action of aromatic amines. For example, with aniline, the reaction may be represented as

$$C_6H_5NH_2 + 2H \longrightarrow C_6H_6 + NH_3$$

Later, while investigating the ignition temperatures of some hydrocarbons in oxygen, Lewis found that the conditions which were necessary for the explosion of such mixtures on progressive heating were sufficiently rapid rise in temperature and an adequate concentration of oxygen, and a concentration of oxygen above a certain minimum, which minimum value increases rapidly with the molecular weight of the hydrocarbon. To obtain ignition with unsaturated hydrocarbons it is necessary that they be present in high concentrations and be heated rapidly. With a bulb of 225 cc. capacity a heating rate of about 1° C. per minute was usually sufficient, though at this rate all concentrations of diisoamyl failed to ignite. Increasing the rate of heating tended to raise the ignition temperature by "superheating", particularly in the case of the paraffins, though the effect was much less marked with the olefins. As shown by the data in Table 148, no distinction was observed between the minimum ignition temperature and the critical inflexion temperature.

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[19] *J.C.S.*, 1927, 155; *ibid.*, 1930, 58.

TABLE 148.—*Relation of the Minimum Ignition Temperature to the Critical Inflexion Temperature.*

Hydrocarbon	Minimum Ignition Temperature ° C.	C. I. T. ° C.
n-Pentane	255–257	255
n-Hexane	232–233	230
n-Heptane	218–220	209
n-Octane	203–204	197
Amylene	241–242	240

It was also suggested that the successive stages in the combustion of paraffins were: (1) primary dehydrogenation, to yield unsaturated hydrocarbons, (2) combination of the unsaturated hydrocarbons with oxygen to form unstable peroxides, and (3) decomposition of peroxides to yield aldehydes which could be further oxidized to water and the oxides of carbon.

Powdered glass and pumice or metals such as platinum, silver, lead and copper increased the ignition temperature of the hydrocarbons. Tin, zinc or aluminum had no effect. Charcoal caused an increase for the paraffins but a decrease for the olefins. Lead tetraethyl caused a marked increase in every case, though its effectiveness rapidly reached a maximum, about 3 to 4 per cent in the case of octane.

Masson and Hamilton[20] used what might be termed the crucible method for the determination of ignition temperatures. A circular platinum plate containing an indentation is welded to the hot junction of a platinum-platinum 10 per cent rhodium thermocouple. The cold junction is placed in a thermos bottle filled with ice to maintain a temperature of 0° C. Heavy platinum wires are welded to the plate and serve as conductors for the alternating current employed in heating the plate. The plate is placed inside the furnace, also heated with alternating current. There is a nickel coil through which dry air is delivered to the plate to remove the products of combustion. The furnace is closed with an alundum top containing a "look tube" with a magnifying glass focused on the platinum plate, and a quartz tube through which the liquid was allowed to drop. An ordinary hypodermic needle was used to obtain drops of constant size.

In making measurements the furnace was first heated until a flash appeared 1 second after the drop of liquid fell on the plate. The temperature of the furnace was then lowered about 10° F. and held constant. The temperature of the plate was raised very slowly until ignition again took place. The temperature of the plate was next raised 15° to 20° F. above this value and then slowly decreased until ignition again just took place. In this way it was possible to obtain readings which could be duplicated within 1° F. Readings were made also of the cooling effect of a drop of liquid on the plate and the rise in temperature which results from surface combustion. A stream of dry air was used to remove the products of combustion after each experiment, but during an actual determination no movement of air over the plate was permitted.

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[20] *Ind. Eng. Chem.*, 1927, 19, 1335; *ibid.*, 1928, 20, 813.

With this apparatus the ignition temperatures of about 80 organic substances were determined. These substances included aromatic and aliphatic hydrocarbons, alcohols, aldehydes, ketones, acids, esters, ethers, amines, and halogen and other derivatives. For a particular class of compounds, normal paraffin hydrocarbons, for example, the ignition temperatures generally decreased with the molecular weight but this decrease was not progressive. Substances of widely different structures and compositions exhibited similar ignition temperatures.

The surface was found to have an effect on the ignition temperature. Surfaces of materials which are known to be catalytically active, contrary to expectations, except in a few instances, gave higher ignition temperatures. This was brought out particularly by the comparison of platinum with glass surfaces, though silver and gold ones were also used.

Bridgeman and Marvin[21] showed that the ignition temperature of a liquid fuel depends upon the material and volume of the vessel used, the concentration of oxygen in the mixture, the lag on ignition, the pressure in the system, and the composition of the fuel. As no test has been devised yet which is standardized with respect to all these variables, results obtained with the same substance by different investigators may vary widely.

Experiments carried out by Bridgeman and Marvin in a bomb indicated that the time required to produce firing depended upon the rate at which heat is received from or lost to the container. Ignition temperatures which involve a lag before ignition, are composite functions of several properties of both the fuel and the apparatus. Actual firing is usually caused by an increase in the temperature of the charge above that of the container, as a result of heat generated in the charge itself. Such ignition temperatures are appropriately called auto-ignition temperatures. The temperature at which instantaneous ignition (without any lag) occurs is the true ignition temperature and is a fundamental property of a given fuel under definite conditions of pressure and concentration.

Compression methods appear to be best adapted to the study of such ignition temperatures. When the charge is adiabatically compressed, the heating is very uniform throughout the charge and the resulting mean temperature can be calculated from the initial conditions and the compression ratio. Ignition in a mixture immediately following adiabatic compression should therefore permit a close approximation to the true ignition temperature.

Closely allied with the ignition of gases by hot surfaces is that produced by heated wires, metallic bars, and similar heated units. The extent to which the glowing filament of a 2-volt miner's electric lamp might be the source of danger in coal mines when the bulb was broken in such a manner as to leave the filament intact has been investigated by Shepherd and Wheeler.[22] The thicker the wire, the lower is the temperature to which it must be heated to cause ignition of mixtures of air and methane.

Mixtures of natural gas (93.2 per cent methane) and air are more easily ignited by wide metallic bars, when heated, than by narrow bars.[23] With platinum it was necessary to heat to a higher temperature than with nickel.[24] This temperature difference in some instances amounted to several hundred degrees. With nickel, tungsten and certain steels, the ignition temperature rose regularly with increasing natural gas content, but with platinum the most explosive mixtures required the highest temperatures. With molybdenum the ignition temperatures of the gas mixtures decreased with increasing natural gas content. This abnormality, however, was probably associated with the burning of the metal, as dense clouds of molybdenum oxide were observed.[25] Moderate turbulence of the gas decreased the ignition temperature, probably by bringing the inflammable gas into the zone of the burnt-out gases and thus raising its temperature. When turbulence was sufficiently great, however, the opposite result was produced.

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[21] *Ind. Eng. Chem.*, 1928, **20**, 1219. This reference gives a review of the work of more than thirty investigators on the ignition temperature of liquid fuel by different methods.

[22] *Safety in Mines Research Board* (*London*), 1926, Paper No. 36, 3; *Chem. Abs.*, 1928, **22**, 167; *Brit. Chem. Abs.* **B**, 1927, 803.

[23] Coward and Guest, *J.A.C.S.*, 1927, **49**, 2479.

[24] *Cf.* Masson and Hamilton, *loc. cit.*

Hot-wire ignition curves were obtained by Schaad and Boord [26] for n-propyl, n-butyl, and isoamyl alcohols, toluene, isoamyl acetate, kerosene, diethyl maleate, and diethyl fumarate between the lower and upper limits of inflammability. The fuel-air mixtures were produced by bubbling air first through the liquid fuel kept at definite temperature (the saturator) and then through the same fuel in the bottom of an ignition tube. Both the saturator and ignition tube were kept at the same temperature. The fuel-air mixture then passed directly in contact with a hot wire.

Curves for ignition amperage plotted against the temperature of the saturator first decreased rather rapidly until a minimum was reached, and then rose again as the upper limit (higher saturator temperature) of inflammability was approached. This minimum temperature differed with the individual fuels. The addition of knock suppressors, such as lead tetraethyl, selenium diethyl, and aniline, increased the lowest temperature required for normal ignition. This increase, measured by current flow, varied from 9.5 to 2.0 amperes, depending upon the knock suppressor added. On the other hand, knock inducers, such as nitrobenzene or isoamyl nitrite, lowered the amperage required for ignition. This lowering varied from 0.15 ampere for nitrobenzene in isoamyl acetate to 1.0 ampere for propyl nitrite in toluene.

Pre-ignition combustion curves were obtained also by using filament currents less than that required for ignition and plotting these against the quantity of carbon dioxide formed. Very little if any carbon monoxide was produced. Without exception, the addition of knock suppressors to the fuels effected a decrease in the pre-ignition combustion, but the addition of a knock inducer caused a marked increase.

IGNITION BY ELECTRICAL DISCHARGE

The relative ease of ignition of a series of methane-air mixtures was measured by Wheeler.[27] He determined the minimum current required to ignite the mixtures.[28] In testing 28 mixtures of methane and air, which contained from 5.85 to 11.50 per cent methane, it was found that the relative igniting current varied from 1.2 amperes for the 5.85 per cent mixture to a minimum of 0.585 ampere for an 8.20 per cent mixture and then rose again to 1.56 amperes for the 11.50 per cent mixture. A plot of the percentage of methane against current yielded a smooth curve. Mixtures of methane and air in which the initial speed of flame propagation was fastest contained from 9.5 to 10 per cent methane, and the most easily ignited mixtures contained 8.2 to 8.3 per cent methane.

The relative ease of ignition of methane-air mixtures with induction sparks (low tension "break-flashes" or momentary arcs) was also investigated.[20] An induction spark differs from a capacity spark principally in its longer duration.

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[25] *Cf.* these results with molybdenum and tungsten with those obtained by Shepherd and Wheeler (*loc. cit.*) with tungsten.

[26] *Ind. Eng. Chem.*, 1929, **21**, 756.

[27] *J.C.S.*, 1920, **117**, 903.

[28] *Cf.* Thornton, *Phil. Mag.*, 1920, **40**, 305; *Chem. Abs.*, 1920, **14**, 3796; Paterson and Campbell, *Proc. Phys. Soc.*, 1919, **31**, 193; *Chem. Abs.*, 1919, **13**, 1970.

[29] Wheeler, *J.C.S.*, 1925, **127**, 14.

This difference was great enough to make it important to determine whether induction sparks were to be regarded as momentary sources of heat or as sustained sources, such as heated surfaces. The results of an extensive investigation indicated, however, that as far as paraffin hydrocarbons were concerned, inductance sparks could be considered similar in effect to capacity sparks, in spite of the wide difference in the two types, both as regards duration and volume. The longer duration and larger volume of the inductance sparks apparently mask small differences in the ease of ignition of those mixtures which are most readily ignited.

Some information regarding the chemical action which takes place during the ignition of methane by the electric spark discharge was obtained by Coward and Meiter.[30] They observed that the spark from an induction coil starts the general inflammation of readily ignitible mixtures of methane and air (8 to 9 per cent methane) when discharged between bluntly pointed platinum electrodes, 0.5 mm. apart. This spark was of sufficient strength to inflame just over 0.5 cu. mm. (measured at ordinary temperatures and pressures) of the mixture. With other mixtures this quantity varied, ranging from 1.5 cu. mm. for a 6.2 per cent mixture to 1.0 cu. mm. for an 11.2 per cent mixture. The spark from an air condenser, which consisted of but one flash, had to inflame only about 0.9 cu. mm., of the most readily ignitable mixtures, to induce general inflammation.

For any given methane-air mixture, with a current of the primary of the induction coil which was less than that required for ignition, it was observed that the extent of the reaction which took place was very nearly proportional to the square of the current. The reaction products contained a large quantity of carbon monoxide and hydrogen, even when a large excess of oxygen was present. It was therefore concluded that the methane-air flame, started by a spark discharge, was propagated from the vicinity of the spark by the heats of reaction of

$$CH_4 + O_2 \longrightarrow CO + H_2 + H_2O\text{ (gas)} + 65{,}000\text{ cal.}$$
$$2H_2 + O_2 \longrightarrow 2H_2O\text{ (gas)} + 116{,}000\text{ cal.}$$

The methane flame appeared to have a small thickness, the first lamina of which included chiefly the formation of carbon monoxide and water vapor and the last lamina, principally the formation of carbon dioxide.

The observed volumes of gas which must be ignited in order to start general inflammation were shown to agree approximately with the known facts concerning the energy of the igniting spark, and the thermal conductivity and ignition temperature of the mixture. Hence, it appears as if the electric spark acts mainly, if not entirely, as a source of thermal energy in igniting a gas mixture.

With a new apparatus of the make-and-break type, developed for the ignition of gaseous mixtures at high temperatures and pressures, Cooper and Wiezevich[31] investigated the upper explosive limits of oxygen-methane mixtures at total pressures from 1 to 229 atmospheres, and at temperatures between 10° and 530° C. It was found that the lower the oxygen concentration, the higher the pressure required for successful ignition. For example, at 20° C., as the total pressure was increased from 1 to 170 atmospheres, the proportion of oxygen in the limit mixture decreased from 39 to 11 per cent. Similarly, rise in temperature was accompanied by a decrease in the proportion of oxygen required for ignition. Spontaneous reactions occurred above 400° C. for the pressure ranges investigated. Complete consumption of the oxygen in the mixture did not take place during explosions at high pressures.

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[30] *J.A.C.S.*, 1927, 49, 396.
[31] *Ind. Eng. Chem.*, 1929, 21, 1210.

In extending their work to the use of break-spark ignition, Schaad and Boord[32] obtained curves similar to those with hot-wire ignition. The minimum currents required to ignite various fuel-air mixtures were not as great with the break-spark ignition as with the hot-wire ignition. The minima of break-spark ignition curves were very close to those temperatures required for combustion to carbon dioxide, but the minima of the hot-wire ignition curves corresponded very closely to the calculated temperatures at which combustion of the fuel would yield principally carbon monoxide. The presence of knock-suppressors or knock-inducers had very little effect. This seemed to indicate that with hot-wire ignition a burn-out occurred in the vicinity of the heated wire before the current required for ignition was reached, and that this effect was practically absent when ignition was effected by a break-spark. Since this burn-out apparently took place when the amperage was less than that required for ignition it might be considered as preliminary or "pre-ignition" combustion. Knock-suppressors, therefore, seemed to hinder this pre-ignition combustion, but knock-inducers promote it.

INCREASE OF PRESSURE DURING COMBUSTION

The pressures developed with mixtures of air and the first five members of the paraffin series when ignited centrally in a spherical bomb have been measured by Maxwell and Wheeler.[33] In all instances, the pressure rise increases with increasing quantities of hydrocarbon in the gas mixtures, reaching a maximum with mixtures containing slightly more hydrocarbon than that required for complete combustion. Beyond this maximum, the rise in pressure decreases with increasing hydrocarbon content.[34] Similar observations were made of the time required for the pressure to develop after ignition and the time required for the maximum pressure to develop. Some of the data obtained by Maxwell and Wheeler with methane-air and butane-air mixtures are given in Tables 149 and 150:

TABLE 149.—*Pressure Developed in Ignition of Methane-Air Mixtures.*
Theoretical mixture for complete combustion: 9.74% CH_4.
Approximate limits of inflammability: 5.6 to 13.6% CH_4.

Methane Per Cent	Time from Ignition to First Indication of Pressure Sec.	Time from Ignition to Maximum Pressure Sec.	Maximum Pressure (Atmos.)
6.05	0.167	0.545	2.67
7.35	0.058	0.119	5.69
10.20	0.020	0.067	7.43
11.90	0.045	0.102	6.54
13.40	0.166	0.368	4.23

Calculated pressures were always higher than observed pressures, the closest agreements being obtained with maximum-pressure mixtures. The discrepancies were believed to result principally from errors in the values of the specific heats of the gases formed during combustion. The mean temperature of the explosion was considered as the principal factor in determining the mean rate of the development of pressure. There was a general agreement between

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[32] *Loc. cit.*

[33] *J.C.S.*, 1927, 2069.

[34] Fenning (*Phil. Trans.*, 1926, **225A**, 331; *Brit. Chem. Abs.* **B**, 1926, 258) reported that under an initial pressure of 95 pounds per square inch and a temperature of 100° C. a maximum pressure was obtained with a 9.7 to 10.5 per cent methane-air mixture and a minimum of "explosion time" with 9.7 per cent methane.

TABLE 150.—*Pressure Developed in Ignition of Butane-Air Mixtures.*
Theoretical mixture for complete combustion: 3.12% C_4H_{10}.
Approximate limits of inflammability: 1.65 to 5.7% C_4H_{10}.

Butane Per Cent	Time from Ignition to First Indication of Pressure Sec.	Time from Ignition to Maximum Pressure Sec.	Maximum Pressure (Atmos.)
2.05	0.078	0.149	5.20
3.00	0.027	0.059	8.15
3.75	0.027	0.057	8.59
4.40	0.041	0.080	7.78
5.15	0.136	0.221	5.83

the composition of the maximum-speed mixtures of hydrocarbons and air, i.e., mixtures of paraffin hydrocarbons and air which give the maximum speed of uniform movement of flame, as determined by Mason[35] and those found by Maxwell and Wheeler. It was concluded that the law of speeds as applied to flame movements in tubes was also applicable to the rate of spread of the flame in a closed spherical container.

Results obtained with mixtures of the olefins, ethylene, propylene or butylene, with air were similar to those obtained with paraffins.[36] This can be seen from the figures in Table 151 which were taken from the data given by Maxwell and Wheeler for propylene-air mixtures.

TABLE 151.—*Pressure Developed in Ignition of Propylene-Air Mixtures.*
Theoretical mixture for complete combustion: 4.44% C_3H_6.
Approximate limits of inflammability: 2 to 8% C_3H_6.

Propylene Per Cent	Time from Ignition to First Indication of Pressure Sec.	Time from Ignition to Maximum Pressure Sec.	Maximum Pressure (Atmos.)
3.18	0.059	0.098	5.69
3.82	0.023	0.060	7.20
4.64	0.023	0.044	7.48
5.67	0.026	0.046	7.66
6.89	0.056	0.113	7.05
7.65	0.115	0.380	5.18

A study of the oxidation of pentane with air under pressure and between the temperatures of 20° C. and 300° C. was made by Dumanois and Mondain-Monval.[37] The air and pentane were introduced at a pressure of 5.3 kg. per sq. cm. into a rotating steel bomb of 700 cc. capacity. The pressure-temperature curves indicated that ignition did not take place below 300° C. if the quantity of pentane was 5 to 10 per cent less than that theoretically required for complete combustion, though a slight increase in pressure[38] was noted at 250° C. With a volume of pentane equivalent to the theoretical quantity required for complete combustion (0.5 cc.), the pressure-temperature curves were almost linear, though a slight break was noted at 120° C. Beyond this and up to about 10° to 15° C. below the ignition temperature, the pressure increased rapidly. The ignition temperature decreased from 238° C. to about 220° C. with increasing proportions of pentane. The explosions also became less violent with increasing quantities of pentane. The pressure-temperature curve for pentane-nitrogen mixtures was steeper but showed no break.

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[35] *J.C.S.*, 1923, **123**, 210.

[36] Maxwell and Wheeler, *J.C.S.*, 1929, 245.

[37] *Compt. rend.*, 1928, **187**, 892; *Brit. Chem. Abs.* **B**, 1928, 917; *La Rev. Petrol*, Nov. 1928, 1568; *Ann. office nat. comb. liquides*, 1928, **3**, 761; *Chem. Abs.*, 1929, **23**, 2694. See also Mondain-Monval and Quanquin, *Bull. soc. ind. Mulhouse*, 1930, **96**, 265; *Brit. Chem. Abs.* **B**, 1930, 803.

[38] *Cf.* Lewis, *loc. cit.*

The presence of 0.11 per cent lead tetraethyl in the pentane-air mixtures caused spontaneous ignition below 300° C. only when the proportion of pentane was greater than that required for complete combustion. Ignition was preceded by a slight increase in pressure and took place at temperatures which were somewhat higher than in the absence of the lead tetraethyl. The curves for benzene under the same experimental conditions failed to exhibit any breaks, and ignition did not take place below 300° C.

When gasoline was substituted for pentane four types of reaction were noted. No spontaneous ignition took place when less than 0.35 cc. was used. With 0.35 to 0.8 cc., violent explosions, accompanied by marked rises in temperature, occurred when the temperature of the bomb reached 220° to 225° C. With 0.8 to 3.6 cc. of gasoline the sudden increases in pressure occurred at gradually decreasing temperatures, although the magnitude of the effect at first diminished, passed through a minimum, and then again increased rapidly. In this third phase it was noted that carbon deposition took place in the bomb. When more than 3.7 cc. of gasoline were used the pressure and temperature increases fell to an even lower value, and were approximately constant for the higher concentrations of hydrocarbons. No carbon deposit was noted in the bomb. These stages corresponded to a discontinuity in the composition of the combustion gases, and also to the different appearances of the flame in the bomb.

To obtain some information with regard to the mechanism of the reactions, hydrocarbon-air mixtures were passed at atmospheric pressure through a heated tube and the oxidation products examined. Reaction began at 160° C. and proceeded rapidly at 300° C., with the production of carbon dioxide, alcohols, aldehydes, and acids. No true ignition was observed even at 360° C. It was concluded that the initial reactions in the bomb were of a similar nature, were exothermic, and were unaccompanied by a flame. Because of their exothermic nature, the temperature of the mixture rises and, if the concentration of the hydrocarbon is sufficiently high, ignition takes place.[39]

When a mixture of pentane and air was heated under pressure at constant volume, Dumanois and Mondain-Monval[40] observed that the sudden rise in temperature and pressure was accompanied by the formation of carbon dioxide and aldehyde. At 230° C. spontaneous explosion of the mixture occurred. The aldehyde was still present in appreciable quantities but the carbon dioxide was not. Analogous results were obtained with hexane, octane, and commercial gasoline. With gasoline it was noticed that unsaturated hydrocarbons were formed during the stage in which no deposition of carbon took place in the steel bomb.[40]

On passing a gaseous mixture of air and pentane (less than 2.5 per cent) at the rate of 6.5 liters per hour into a glass receiver which was heated progressively to 800° C. in such a manner that the products of oxidation were not removed, Prettre, Dumanois and Laffitte[41] observed that a luminescence appeared at 250° to 300° C., and ignition took place at 670° C. With a larger proportion of pentane (up to 13 per cent) luminescence was noticed at 259° to 263° C., depending upon the composition of the gas mixture, and ignition occurred at 670° to 680° C. It was concluded by them, from the changes in the nature of the luminescence that two spontaneous ignitions occur, one at 260° to 300° C.

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[39] See also Mondain-Monval and Quanquin, *Ann. combustibles liquides*, 1930, **5**, 307; *Chem. Abs.*, 1930, **24**, 5714.

[40] *Compt. rend.*, 1929, **189**, 761; *Brit. Chem. Abs.* **A**, 1930, 57. *La Rev. Petrol*, Nov. 2, 1929, 1550; *Ann. combustibles liquides*, 1929, **4**, 1069; *Chem. Abs.*, 1930, **24**, 3210.

[41] *Compt. rend.*, 1930, **191**, 329; *Brit. Chem. Abs.* **A**, 1930, 1255.

and the other above 660° to 670° C. In the interval 300° to 600° C. the mixtures do not ignite but only luminesce.

Brown, Leslie and Hunn[42] showed that the rate of increase of pressure in a gaseous explosion is dependent not only on the rate of the chemical reactions, but also on the initial temperature of the mixture. The fuel used in their investigations was a petroleum fraction boiling between 66.9° and 67.4° C., and consisted principally of isohexane. A measured quantity of the fuel together with the desired amount of oxygen and nitrogen was placed in a constant-volume bomb, and the mixture heated to a given temperature. The mixture was then ignited by an electric spark and the changes of pressure with time were recorded photographically by a camera (Midgley indicator[43]). When the fuel was present in excess, increases in initial temperatures resulted in increases in the rate of rise of pressure until a temperature of 75° C. was reached. Above this temperature the rates decreased. When the air or oxygen was in excess no such critical temperature was noticed at room temperature or above.

Carr and Brown[44] determined the rate of pressure increase of explosive mixtures of different types of hydrocarbons containing varying amounts of lead tetraethyl. The effect of this compound was found to be essentially independent of the chemical structure of the fuel but was governed by the type or rate of combustion of the explosive mixture. When the rate of reaction or rise in pressure increased, the retarding action of the lead tetraethyl decreased and an accelerating effect on the combustion was noted. A similar effect was observed on varying the quantity of lead tetraethyl added to the explosive mixture. Small quantities of this substance tended to retard slow combustion. Larger quantities had no retarding action, but produced, in many instances, an actual accelerating effect.

In attempting to explain this action, Carr and Brown assumed that, in slow-burning mixtures, the decomposition products of lead tetraethyl were the active agents. In rapid-burning mixtures, the rate of inflammation is greater than that of the decomposition of lead tetraethyl, the latter therefore does not have time to form those products which retard the flame. The accelerating action of the lead tetraethyl may be due to the explosive decomposition which occurs in the flame front or possibly to the positive catalytic action of some intermediate decomposition products such as free ethyl radicals.

This accelerating effect resulting from the addition of large proportions of antidetonating substances was pointed out also by Grebel.[45] When iron carbonyl, ethyl fluid (50 per cent lead tetraethyl and 50 per cent ethyl bromide), or aromatic compounds such as benzene or nitrobenzene, were added in small quantities to gasoline, ignition temperature increased, but when added in large amounts, the ignition temperature decreased.

FLAME PROPAGATION

While investigating the mechanism of the ignition of gases by means of an electric spark Wheeler[46] observed that the most readily ignitible mixture of methane and air contained a greater percentage of air than was required for complete combustion, but the reverse was true for mixtures of the higher paraffins and air. Some of the results obtained are given in Table 152.

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[42] *Ind. Eng. Chem.*, 1925, 17, 397.

[43] *J. Soc. Automotive Eng.*, 1920, 7, 491.

[44] *Ind. Eng. Chem.*, 1929, 21, 1071.

[45] *Compt. rend.*, 1929, 189, 90; *Chem. Abs.*, 1929, 23, 5311.

[46] *J.C.S.*, 1924, 125, 1858. In an addendum to this work, S. C. Lind has pointed out that the rate of reaction between a combustible gas and oxygen increases with the concentration of whichever gas has the greatest stopping power for the radiant energy which will activate it, and its stopping power depends upon the density of the gas.

TABLE 152.—*Ignition Characteristics of Hydrocarbon-Air Mixtures.*

Gas	Mixture in Which Speed of Uniform Movement of Flame is Fastest	Mixture for Complete Combustion	Mixture Most Readily Ignited by Secondary Discharge
	Per Cent		
Methane	9.65	9.45	8.3
Ethane	6.05	5.64	6.7
n-Propane	4.45	4.02	5.1
n-Butane	3.65	3.13	4.2
n-Pentane	2.90	2.56	4.0
n-Hexane	—	2.15	3.2

For the propagation of flames in such mixtures it was found that a minimum volume of the mixture must be burned.

It was also observed that mixtures of air and methane varied as regards their sensitiveness to ignition by various means. For example, mixtures most readily ignited by contact with the walls of a heated vessel contained 5 to 6 per cent methane, but those most readily ignited by an electric spark contained 8.25 to 8.50 per cent methane.[47] The ignition temperature was defined as the lowest temperature under the conditions of the experiment at which inflammation took place, regardless of how long the surface remained in contact with the mixture. The ease of ignition of gases by a momentary source of heat, such as an electric spark, was dependent on the normal speed of propagation of flame in the mixture. It had been observed previously that flames spread away from the path of an electric discharge most readily in those mixtures in which the speed of propagation normally is fastest.[48]

With a standardized flame projected vertically downward from a silica jet as a source of ignition, Walls and Wheeler[49] determined what mixtures of hydrocarbons and air were most readily ignitible, the relative speed of the flame, and the relative duration of exposure of the mixture to the source of heat. The data obtained (see Table 153) indicate that ease of ignition corresponds with the ability of the flame to travel through the mixture after the source of ignition is withdrawn.

TABLE 153.—*Characteristics of Hydrocarbon-Air Flames.*

Gas	Mixture in Which Speed of Uniform Movement of Flame is Fastest Per Cent	Relative Speed of Flame (Cm. per Sec.)	Mixture Most Readily Ignited Per Cent	Relative Duration of Exposure to Flame Required (Milliseconds)
Methane	9.65	91	9.8–10.0	4.3
Ethane	6.05	127	6.8–7.0	2.7
Propane	4.45	114	4.8–5.0	3.2
n-Pentane	2.90	115	3.1–3.3	3.5

Wheeler and his collaborators also showed that the time required for the development of the maximum pressure after combustion of gaseous mixtures in a closed system decreases as the flame speed increases.[50] By application of the law of speeds it was possible to calculate the time required for the development of the maximum pressure for various gaseous mixtures.[51]

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[47] Walls and Wheeler, *J.C.S.*, 1927, 129, 291.
[48] Wheeler, *J.C.S.*, 1920, 117, 903; *ibid.*, 1925, 127, 14.
[49] *Loc. cit.*
[50] Maxwell, Payman and Wheeler, *J.C.S.*, 1927, 297.

By means of photographs of moving flames, taken at intervals of 4.58 milliseconds, Ellis and Wheeler [52] showed that flame propagation takes place in regular concentric spheres. These results verified the assumptions previously made by Wheeler,[53] and also the deductions of Mallard and Le Chatelier [54] from time-pressure curves. The rate of propagation of flame was affected by cooling at the walls of the vessel. The pressure at any time is smaller when the point of ignition is at the bottom than at the center of the vessel.

The movement of the flame in a given combustible gaseous mixture is dependent upon several factors: the length and bore of the tube, the position of the spark gap, the initial mechanical turbulence, the intensity of the spark, and the initial temperature and pressure.[55] At any given point in the tube the velocity varies with the length of the tube. With central ignition, flame propagation is symmetrical, but if the ignition is not central, the flame front approaching the nearer end is slower than the other. The speed of the flame increases almost rectilinearly with the width of the spark-gap up to a certain point which is dependent chiefly on the strength of the current in the primary circuit and the winding ratio of the induction coil.

Flame propagation can be divided into two phases: one of which is characterized by regular acceleration and the other by a slow and almost perfectly constant speed. In heated mixtures the initial phase is faster and ends nearer the spark, and the flame is less luminous. Maximum speed is attained at 1 atmosphere pressure. Pressures greater or less than 1 atmosphere are accompanied by decreasing speeds. This is shown by the data in Table 154 for a 6.5 per cent ethylene-air mixture:

TABLE 154.—*Effect of Pressure on Ethylene-Air Flame Speed.*

Pressure Atmos.	Flame Speed Meters per Sec.
0.9	8.79
1.0	8.95
1.1	8.76
1.2	8.38

The influence of an inert gas, such as nitrogen, on the speed of the flame has been studied by Campbell and Ellis [56] and by Ellis and Stubbs.[57] Experiments were made by the former with various oxygen-nitrogen mixtures together with the appropriate quantity of fuel, such as methane, ethylene, carbon disulphide, pentane, hexane, alcohol or ether. The speed in all instances was decreased as the dilution with nitrogen increased. The speed of the flame, however, was proportional to the calorific value of the gas mixture. The latter investigators used mixtures of the type $xC + yE$, in which $C = 1$ molecule of carbon disulphide to 3 molecules of oxygen and $E = 2$ molecules of hydrogen to 1 molecule of oxygen. Ellis and Stubbs observed that when the calorific value of the mixture was constant, the speed of the flame was proportional to the thermal conductivity of the mixture. The thermal conductivity was a product of three quantities: the density, the viscosity and the specific heat.

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[51] The law of speeds is stated by Payman and Wheeler (*J.C.S.*, 1922, **121**, 365) as follows: "Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures of the same type propagate flame at the same speeds, under the same conditions of experiment."

[52] *J.C.S.*, 1925, **127**, 764.

[53] *J.C.S.*, 1918, **113**, 840.

[54] *Ann. mines*, 1883, (8) **4**, 379; see also *Bull. soc. chim.*, 1883, (2) **39**, 268, 369; *Chem. Soc. Abs.*, 1883, **44**, 844; *Compt. rend.*, 1882, **95**, 599, 1352; *Chem. Soc. Abs.*, 1883, **44**, 148, 542; *Bull. soc. chim.*, 1883, (2) **39**, 572; *Chem. Soc. Abs.*, 1884, **45**, 549.

[55] Ellis, *J.C.S.*, 1923, **123**, 1435.

[56] *J.C.S.*, 1924, **125**, 1957.

[57] *J.C.S.*, 1924, **125**, 1960.

Stevens[58] examined the rate of flame propagation in mixtures of carbon monoxide and oxygen. A mixture of these gases, in which the individual partial pressures were known, was employed to blow a soap bubble. Through the aperture from which the bubble was blown was inserted an ignition gap which was extended as near the center of the bubble as possible. After firing, the volume of the bubble was photographed at regular intervals on a continuous film. This gave the initial and final volumes at constant pressure. Under these conditions the concentrations of the gases about to explode remained constant. The flame velocity was found to be constant and proportional to the initial concentrations of the reactants. For example, with carbon monoxide, this can be expressed by

$$S = k\,[CO]^2\,[O_2]$$

in which S is the speed of the flame, and k is a proportionality factor dependent on the vapor pressure of the water present in the gases.

MECHANISM OF COMBUSTION AND THE EFFECT OF KNOCK-INDUCING AND KNOCK-SUPPRESSING COMPOUNDS

The work of Callendar, King and Sims[59] led to the formulation of the nuclear theory of the self-ignition of motor fuels. Briefly, this theory states that the detonation of liquid fuels, at high compression ratios, is due to the presence of nuclear drops or residues of low ignition points and probably to the presence of heavy paraffins since these have the lowest ignition temperatures of any of the constituents of gasolines. The antidetonating properties of lead tetraethyl and nickel or iron carbonyl, and the pronounced effect which results from the presence of relatively small quantities, was attributed to the reducing action of the metals, formed by decomposition at high temperatures, which became concentrated in and delayed the action of the nuclear residues. Other substances which exhibited antidetonating properties were aromatic hydrocarbons, aromatic amines, and alcohols.

Further work on the slow combustion of fuels appeared to confirm this theory.[60] The temperature of initial combustion of a number of organic liquids was determined by passing a mixture of the vapor and air through a glass tube, the temperature of which could be gradually increased. It was observed that nuclei in the form of a dew or fog always preceded or else accompanied the initial stage of oxidation. The products of the reaction included water, carbon dioxide, aldehydes or acids, and traces of "active oxygen." Detonation and the presence of active oxygen became more marked when the fuel was injected into the tube as a fine spray, which phenomena indicated the formation of organic peroxides in the nuclear drops. The small amount of peroxide was not sufficient in itself to cause the detonation, but acted as a primer which effects the simultaneous ignition of the drops. The addition of antidetonants such as lead tetraethyl and others, completely altered the course of the reaction. Antidetonants inhibited the formation of active oxygen among the products of combustion, and thus raised the spontaneous ignition temperature of the mixture.

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[58] *J.A.C.S.*, 1926, **48**, 1896. For other methods of studying flame propagation in inflammable gas mixtures see Ellis and Robinson, *J.C.S.*, 1925, **127**, 760; and Perrott and Gawthrop, *Ind. Eng. Chem.*, 1927, **19**, 1293.

[59] *Engineering*, 1926, **121**, 475, 509, 542, 575, 605; *Brit. Chem. Abs.* **B**, 1926, 618; see also Marek and Hahn, "Catalytic Oxidation of Organic Compounds in the Vapor Phase," Chemical Catalog Co., Inc., New York, **1932**, 302; Kalichevsky and Stagner, "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, **1933**, 269.

[60] Callendar, *Engineering*, 1927, **123**, 147, 182, 210; *Brit. Chem. Abs.* **B**, 1927, 272; *Chem. Abs.*, 1927, **21**, 1697.

In investigating the reactions taking place during the combustion of fuels, Mardles[61] employed two experimental methods. In the first, a mixture of air and fuel was passed through a heated tube and the products of the reaction were identified. These products were active oxygen, probably present as organic peroxides, and aldehydes and acids, formed by the decomposition of such peroxides. The addition of substances such as benzene, aniline or lead tetraethyl to the fuel-air mixture effected a marked decrease in the amount of active oxygen produced. In the presence of fuels, both aniline and benzene were oxidized at temperatures much lower than are required for their oxidation alone. This oxidation was shown to be due to peroxides and not to hydrogen peroxide formed by the hydrolysis of the peroxides. Similar results were obtained also by the second method, in which the reactants were placed in a bulb and the rate of reaction was followed by the change in pressure as the temperature was slowly raised. This experimental work confirmed the views of Callendar.

The results of Berl and Werner[62] on the ignition of mixtures of ethylene or methane with insufficient air for complete combustion but under just sufficient pressure for reaction to take place led them to conclude that combustion results in the preferential oxidation of the hydrogen. On increasing the pressure, however, the proportion of carbon dioxide and especially of carbon monoxide formed increases rapidly, For example, of the oxygen present in a 40 per cent ethylene-air mixture, 83 per cent appeared as water, 3 per cent as carbon dioxide, and 14 per cent as carbon monoxide after ignition under 40 atmospheres pressure. Under 92 atmospheres pressure, 50 per cent of the oxygen appeared as water, 10 per cent as carbon dioxide, and 40 per cent as carbon monoxide after ignition.

The ignition temperatures of mixtures of the inflammable vapors of motor fuels and air, at pressures varying from 1 atmosphere to 20 atmospheres, and the influence of knock-suppressing compounds on these temperatures was investigated by Berl, Heise and Winnacker.[63] In the case of mixtures of air and hydrocarbons such as n-pentane, n-hexane, and cyclohexane, an increase in pressure had only a very slight effect in depressing the ignition temperature. With a mixture of ether vapor and air, the effect of pressure was somewhat greater. With mixtures of air and benzene or alcohol vapor, ignition did not occur at 800° C. under the pressures investigated. Cyclohexene at 60° C. and under 20 atmospheres pressure was polymerized by the oxygen in the air. In general, those substances which were the most easily oxidized also caused knocking the most readily. The addition of knock-suppressors, such as lead tetraethyl or iron carbonyl, raised the ignition temperature to approximately the same extent. The compression strength was found to increase according to the series: hexane, cyclohexane, cyclohexene, benzene.

Experiments by Butkov[64] also confirmed the view that those hydrocarbons which have a pronounced tendency to knock are readily oxidized. The heavy ends of gasoline, which have a high knock value are comparatively easily oxidized. Butkov suggested that two types of oxidation were involved: an explosive reaction resulting in the formation of water, carbon monoxide and dioxide and a non-explosive reaction which yields asphalt-like materials and acids. The second type is characteristic of heavy hydrocarbons and takes place at relatively low temperatures.

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[61] *J.C.S.*, 1928, **130**, 872.

[62] *Z. angew. Chem.*, 1927, **40**, 245; *Brit. Chem. Abs.* **B**, 1927, 546. See also Berl, *Chimie et industrie*, 1929, **21**, 452; *Brit. Chem. Abs.* **B**, 1929, 419.

[63] *Z. phys. Chem.*, 1928, **139**, 453; *Brit. Chem. Abs.* **B**, 1929, 158; *Chaleur et ind.*, 1929, **10**, 179, 241; *Chem. Abs.*, 1931, **25**, 806; *Z. phys. Chem.*, 1929, **145**, 161; *Chem. Abs.*, 1930, **24**, 4143.

[64] *Izvestiya Teplo-Tekh. Inst.* (*Trans. Thermo-Tech. Inst. Russia*), 1930, No. 2, 41; *Chem. Abs.*, 1931, **25**, 406.

Oxidation of hydrocarbons in the presence of an insufficient quantity of oxygen for combustion was also investigated by Berl, Heise and Winnacker,[65] as well as the effect of knock suppressors such as lead tetraethyl and iron carbonyl. The antiknock metallic compounds proved to be powerful inhibitors for the conveyance of oxygen, their action being attributed to decomposition into finely divided metals.[66] A similar but less pronounced effect was obtained with finely divided lead and iron in a luminous arc. The finely divided metals arrest oxidation of the hydrocarbon molecules by interrupting the chain reactions or by forming compounds with the peroxides which result. Hydrocarbons which were rich in hydrogen were decomposed into hydrogen and an unsaturated hydrocarbon, both of which were then oxidized to form water, hydrogen peroxide, and organic peroxides. The finely divided metals inhibited this latter peroxide formation before the succeeding intramolecular oxidation could take place.

Egerton,[67] as well as Weerman,[68] showed that antidetonating substances raise the ignition temperature of gasoline in air. Weerman observed that the metallic vapors which were most effective in increasing the ignition temperature fell in the following order: thallium, potassium, lead, iron, nickel, manganese, bismuth, selenium, tellurium, sodium, cadmium, calcium, and antimony. The ineffective elements were aluminum, magnesium, mercury, iodine, phosphorus, gold, and zinc. The effect of the following metals was doubtful: tin, cerium, titanium, zirconium, thorium, tantalum, tungsten, chromium, cobalt and uranium. Weerman stated that, in general, a state of equilibrium exists between certain products of the antiknock at the temperature at which they operate.[69] For example, with potassium there is an equilibrium between the oxides, K_2O_3 and K_2O_4, in favor of the higher oxide at 400° C. Any reduction to the lower state is followed by a regeneration to the higher state by the next suitable impact with an oxygen molecule. Peroxide formation with the production of centers of high energy content is regarded as the initial stage in the combustion of a hydrocarbon molecule, and the antiknock substances inhibit oxidation of the fuels prior to ignition.[70]

Berl and Winnacker suggested that with decrease in symmetry of a combustible molecule, as a result of its combination with oxygen, it becomes more readily oxidized. Thus, the oxidation of hexane, a symmetrical molecule, is preceded by an induction period[71] during which small quantities of oxygenated products, aldehydes and acids, are formed. These unsymmetrical oxygenated products add oxygen more readily than the symmetrical hydrocarbon molecules, and they therefore act as autoxidizers towards the hydrocarbon molecules.

This theory appeared to be substantiated by the results obtained on the oxidation of benzaldehyde.[72] The rate of autoxidation of liquid benzaldehyde was measured at ordinary temperature, the reaction being followed by the direct measurement of the rate of absorption of oxygen. In the experiments, the oxidation of benzaldehyde proceeded at a rapidly increasing rate after the expiration of a period of induction. On adding benzoic acid to the benzaldehyde, a longer period of induction was observed as well as a decrease in the maximum reaction velocity which was attained. Benzoyl peroxide, on the other hand, shortened the induction period and increased the maximum reaction velocity. Benzene, hexane, acetone, cyclohexane, ether, cyclohexene, ethyl alcohol, benzyl alcohol, and lead tetraethyl retarded the reaction, the effects increasing in that order, either by preventing the formation of peroxides or by reacting with them. Sols resulting from the dispersion of lead, tin or iron in benzaldehyde also diminished the capacity for oxidation.

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[65] *Loc. cit.*

[66] *Cf.* Carr and Brown, *Ind. Eng. Chem.*, 1929, **21**, 1071; also Egerton and Gates, *J. Inst. Pet. Tech.*, 1927, **13**, 244.

[67] *Proc. Roy. Inst. Gt. Brit.*, 1928; *Chem. Abs.*, 1928, **22**, 3521; *Nature*, 1928, **121**, 10; *Chem. Abs.*, 1928, **22**, 1034.

[68] *J. Inst. Pet. Tech.*, 1927, **13**, 300; *Chem. Abs.*, 1927, **21**, 2555.

[69] Egerton, *loc. cit.*

[70] Berl and Winnacker, *Z. phys. Chem.*, 1930, **148**, 36; *Brit. Chem. Abs.* **A**, 1930, 1002.

[71] *Cf.* Brunner and Rideal, *J.C.S.*, 1928, 1162.

[72] Berl and Winnacker, *Z. physik. Chem.*, 1930, **148**, 261; *Brit. Chem. Abs.* **A**, 1930, 1002

Taylor,[73] who also observed a decreased rate of oxidation of benzaldehyde in the presence of lead tetraethyl, suggested that not only the lead atoms but also the free radicals function as oxidation centers. These free radicals, ethyl in the particular instance, are very active in the presence of hydrocarbon-oxygen mixtures. Free radicals possibly act as oxidation centers, producing homogeneous combustion which would be supplementary to the inhibitory action of the metal alkyl on the oxidation of the aldehydes produced by the partial oxidation of the hydrocarbons. The action of free radicals may also account for the inhibitory action of antiknocks of the non-metallic type, such as aniline.[74]

Graetz[75] concluded that any thermal dissociation reaction is preceded by the autoxidation of the gasoline, which occurs mainly in the liquid phase and at an optimum temperature of 120° to 160° C. The most readily autoxidizable hydrocarbons are those of the ethylene series (C_2H_4 and homologues), and these may yield either unstable and detonating compounds or stable compounds. The presence of a large proportion of ethylene hydrocarbons in gasolines effects a more regular autoxidation of the paraffin hydrocarbons and leads to more stable or easily hydrolyzed products. The antiknock properties of aromatic compounds can be attributed to the stability of the peroxides which they form. This stability, however, renders them less appropriate as catalysts for the oxidation of paraffin hydrocarbons. They can combine directly with unsaturated compounds and thus act as reagents rather than as catalysts. Graetz stated that they must be present in large quantities (50 per cent or more) in order to produce beneficial effects. Ketones and aldehydes, particularly cyclohexanone and menthone, behave like the ethylene hydrocarbons. The two chief factors which destroy peroxides are water which hydrolyzes them and high temperatures which bring about their decomposition.

Layng and Youker[76] investigated the action of accelerators and inhibitors upon the oxidation of hydrocarbons in both the liquid and the gas phase. The hydrocarbons together with oxygen were introduced into a bulb which was kept at a constant temperature and the reactions were followed by measuring the change in pressure. The data indicated that aniline, diphenylamine, potassium ethoxide and lead tetraethyl were all inhibitors of gas phase oxidation, but sodium and potassium ethoxides and lead tetraethyl were accelerators of liquid-phase oxidation. For a compound, therefore, to act as an antiknock they assert that it must be an inhibitor of gas-phase oxidation and an accelerator of liquid-phase oxidation. Compounds which fail to approach lead tetraethyl but which have some effect as antiknocks seem to exert an action in only one of the phases present in the gas engines at the temperatures employed during the test.

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[73] *Nature*, 1927, 119. 746; *Chem. Abs.*, 1927, 21. 2555.
[74] *Cf.* Lewis. *loc. cit.*
[75] *Ann. office nat. comb. liquides*, 1928, 3, 69; *Chem. Abs.*, 1928, 22, 2459.
[76] *Ind. Eng. Chem.*, 1928, 20, 1048.

The changes taking place during the oxidation of gasoline-air mixtures previous to ignition, both in the absence and in the presence of knock-suppressors, have been studied by Zaikowsky, Holroyd and Sokolov.[77] The untreated mixtures underwent greater oxidation, though there was no corresponding increase of the compression pressure. This indicated that oxidation was not a homogeneous reaction. The addition of lead tetraethyl, or other antiknock compounds, reduced the rate of oxidation in the gas phase for a short time, and the metallic oxides which were deposited were effective antioxidizing agents. Lead oxide was a positive surface catalyst for carbon. The effectiveness of antiknock compounds was attributed to their temporary elimination of oxygen molecules which are activated sufficiently to react directly with hydrocarbons.

The combustion process taking place in gasoline-air mixture was followed by determining the oxygen concentration in the gases withdrawn from different parts of the combustion chamber at various intervals during the combustion of the charge.[78] The results indicated that there was a definite combustion zone which passed through the charge of gasoline and air at a definite velocity. This conclusion was based upon the fact that longer intervals elapsed between the instant of ignition and the start of decreasing oxygen concentration as the distance increased between the point of ignition and the point in the chamber at which the gas was removed. During these intervals, the oxygen concentration in the sample remained fairly constant.

The combustion zone traveled faster through the middle portion of the combustion chamber than along the side walls. This phenomenon was probably a result of the cooling effect of the walls. It was also thought that the flame front, which is convex in the direction of travel, proceeded outward from the point of ignition through all portions of the charge.[79] The speed of the combustion zone, through both the middle portion and along the side walls, was increased by increasing the speed of the engine. This increased speed of combustion was attributed to, at least in part, increased turbulence of the charge. With gasoline, the knocking appeared to be associated with the combustion of the last portion of the fuel. The data seemed to indicate that there was a more rapid speed of the combustion wave through the last quarter of the combustion space in detonating explosions than in non-detonating explosions.

It has been pointed out by Grebel[80] that calculations based on the assumption that combustion goes to carbon dioxide and water are incorrect. The gas mixture in the cylinder is not homogeneous, and its composition does not correspond to a chemical equilibrium. Combustion takes place in stages with the production of aldehydes,[81] acids, carbon monoxide, and other substances. Combustion is catalyzed by the presence of appropriate quantities of some of the products, such as carbon dioxide or water vapor. More efficient operation will result when fuel and air are thoroughly mixed in optimum proportions together with a small quantity of the exhaust gases, as catalyzers.

From a consideration of the analyses of exhaust gases from automobile engines obtained by a number of investigators, Lovell and Boyd,[82] contrary to the views of Grebel, concluded that the components of such gases are in a state of equilibrium which may be represented by

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[77] *Phys. Rev.*, 1929, (2) **33**, 264; *Brit. Chem. Abs.* **B**, 1931, 8.

[78] Withrow, Lovell and Boyd, *Ind. Eng. Chem.*, 1930, **22**, 945.

[79] *Cf.* Ellis and Wheeler, *loc. cit.*

[80] *Chimie et industrie*, 1928, **20**, 813; *Brit. Chem. Abs.* **B**, 1929, 43; *Chem. Abs.*, 1929, **23**, 2011. For the description of a carburetor which first subjects the mixture of fuel vapor and air to the action of a heated catalyst, see Soc. Anon. Le Carbone, British Patent 288,588, 1927; *Brit. Chem. Abs.* **B**, 1928, 805.

[81] For the recovery of products from the exhaust gases of internal combustion engines, see Paris, U. S. Patent 1,388,480, Aug. 23, 1921; *Chem. Abs.*, 1921, **15**, 4047.

[82] *Ind. Eng. Chem.*, 1925, **17**, 1216.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

The equilibrium value, represented by $K = \frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]}$, lies within very narrow limits (from 3.0 to 4.0) and corresponds to an equilibrium reaction at temperatures of 1350° to 1550° C. They also concluded that over 95 per cent of the hydrocarbon was burned to carbon dioxide and carbon monoxide under various conditions during which the engines ran smoothly. The amounts of hydrogen burned to water and carbon burned to carbon dioxide seemed to confirm the hydroxylation theory of combustion of hydrocarbons, and disprove the idea that the maxima of power curves for gasoline engines occurred when 85 per cent of the theoretical air was used because of a preferential burning of hydrogen.

GASEOUS IONIZATION AND KNOCKING

One of the explanations offered for the effects of knock-inducing or knock-suppressing compounds is based on the ionization of gases. It is known that burning gases are conductors of electricity, and therefore are ionized. Part of the energy from the reactions of the molecules in the flame were thought to be used in liberating electrons which then precede the flame front and ionize the combustible mixture just ahead. The higher the temperature and pressure of the reacting gases, the greater would be the velocities of the liberated electrons, and consequently the faster the propagation of the flame, thus causing a larger portion of the charge to detonate. The liberated electrons are absorbed by the lead atoms, hence the effect of the lead tetraethyl on detonation. The negatively charged lead atoms attracted positively charged atoms and discharged them. In this manner one atom of lead would prevent a large number of molecules from being sufficiently activated to bring about detonation. A knock-inducing compound would act in the opposite manner.

Clark, Brugmann and Thee[83] tested this theory by measuring the ionization of air, air-benzene, air-benzene-butyl nitrite (knock-inducer), and air-benzene-lead tetraethyl (knock-suppressor) mixtures. The ionization was affected with monochromatic molybdenum Kα x-rays of constant intensity, and the ionization currents were measured by a very sensitive quadrant electrometer and a gold-leaf electroscope.

The presence of butyl nitrite in an air-benzene mixture slightly increased the total ionization, these results being in accord with the theory. The presence of lead tetraethyl, however, gave a still larger total ionization, which was not according to theory. The presence of butyl nitrite in the benzene-air mixture decreased the rate of recombination, again in accord with the theory, but the presence of lead tetraethyl decreased the rate of recombination to a larger extent. This latter effect again was contradictory to the theory. The experimental evidence, therefore, did not adequately substantiate the theory of gaseous ionization and detonation.

The influence of an antiknock compound on the rate of slow oxidation of methane under the ionizing action of radon was investigated by Lind and Bardwell.[84] The antiknock compound used was diethyl selenium, because of its greater volatility than lead tetraethyl. The results indicated some acceleration but no retarding influence of this compound on the rate of the reaction. These investigators therefore concluded that ionization did not play a primary rôle in the explosive reaction or in the flame propagation.

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[83] *Ind. Eng. Chem.*, 1925, 17, 1226.
[84] *Ind. Eng. Chem.*, 1927, 19, 231.

By means of a delicate electrometer, Gill[85] attempted to measure ionization in fuel vapors during slow combustion in air. No detectable ionization occurred when the vapors of hexane or carbon disulphide were undergoing slow phosphorescent combustion in air at temperatures up to 400° C. Similar results were obtained when substances such as lead tetraethyl or iron carbonyl, which inhibit phosphorescence, were present. With hydrogen-air mixtures appreciable ionization occurred only immediately before self-ignition at relatively high temperatures. The ignition temperature was lowered by the presence of nitrogen peroxide. This cannot be accounted for by ionization effects, as no ionization was detected in the reaction between hydrogen and nitrogen in the absence of air.

ANTIKNOCKS OR KNOCK-SUPPRESSING COMPOUNDS

In the preceding pages various substances have been mentioned which can be used as antidetonants or knock-suppressors. These include ethyl and benzyl alcohols, potassium ethoxide, aromatic compounds (benzene, toluene, and aniline), and organo-metallic compounds (lead tetraethyl and iron carbonyl). Numerous other substances have been suggested and the following examples are given merely to illustrate their wide variety.

Egerton recommended the vapors of thallium or thallium compounds,[86] such as thallium ethyl, ethoxide or oleate. The heavy metal derivatives of β-diketones, such as those of iron, nickel, cobalt, and, as well as the aluminum, zinc, and other metallic compounds of acetylacetone or benzoylacetone or their homologues have been proposed by Coffey.[87] Mercury cyanide has also been suggested.[88] The butyl esters of hydroxynaphthenic acids as well as the mercury compounds of naphthenic acids or their esters have been mentioned.[89] The alkali oleates, naphthenates and sulphonates are said to be antidetonants.[90] The cracking of hydrocarbons in the presence of ammonia, or of nitrogenous organic compounds, in order to produce gasolines containing cyclic nitrogen compounds which are nondetonating was suggested by Brown and Sullivan.[91] Mixtures of various antiknock substances can be used, as for example, a mixture containing aniline, acetone and anhydrous alcohol.[92] The antiknock properties of aromatic amines may be increased by the addition of a substance having a high critical temperature and a high spontaneous inflammation temperature.[93] Such a mixture may consist of aniline and hydrocarbons obtained from coal tar and having a boiling range of 170° to 250° C. "Targol," a mixture of terpenes which have been oxidized with oxygen, has been used.[94] Oxidized kerosene has been proposed as a fuel of much less knocking tendency than straight kerosene for use in kerosene engines.[95] "Brittolizing" of motor fuels is a process which is said to consist in binding ether into any straight-run distillate with the aid of a catalyst to improve its combustion.[96]

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[85] *Trans. Faraday Soc.*, 1930, **26**, 49; *Chem. Abs.*, 1930, **24**, 2858; *Brit. Chem. Abs.* **A**, 1930, 398.

[86] British Patent 279,560, 1926; assigned to Asiatic Petroleum Co., Ltd.; *Chem. Abs.*, 1928, **22**, 3042.

[87] British Patent 287,192, 1926; assigned to British Dyestuffs Corp., Ltd.; *Brit. Chem. Abs.* **B**, 1928, 357.

[88] Du Camp, British Patent 308,610, 1928; *Chem. Abs.*, 1930, **24**, 496; German Patent 520,010, 1926.

[89] Rosenbaum, U. S. Patent 1,841,254, Jan. 12, 1932; *Chem. Abs.*, 1932, **26**, 1768.

[90] Egerton and Barton, British Patent 300,156, 1927; assigned to Asiatic Petroleum Co., Ltd.; *Brit. Chem. Abs.* **B**, 1929, 46.

[91] U. S. Patent 1,797,819, Mar. 24, 1931; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1931, **25**, 2845.

[92] De la Riboisière, French Patent 710,402, 1931; *Chem. Abs.*, 1932, **26**, 1769. Koblitz (British Patent 347,132, 1930; *Brit. Chem. Abs.* **B**, 1931, 750) described the use of a mixture containing aniline, anthracene, camphor, castor oil, various hydrogenated naphthalenes, picric acid, ether, nitronaphthalene and cresol; to this may also be added monochloronaphthalene, acrolein, hydroquinone, and benzoic acid.

[93] Petroff, French Patent 714,241, 1930; *Chem. Abs.*, 1932, **26**, 1769.

[94] Laurent, *Chimie et industrie*, Apr. 1928, Special No. 319; *Chem. Abs.*, 1928, **22**, 4236; *cf. Chimie et industrie*, Special No. 266; *Chem. Abs.*, 1927, **21**, 3444.

Grote[97] showed that those compounds containing tetravalent lead were the best antidetonants, whereas those containing bivalent lead, with few exceptions, possessed little or no antidetonating properties. He states that as a rule the most powerful antiknock materials yield finely divided particles of the metallic constituent on heating, but compounds which undergo complete oxidation on heating are inefficient.

Straight-chain paraffin hydrocarbons show a regular and rapid decrease in antiknock quality as the number of carbon atoms in the chain increases. When the number of carbon atoms in the chain remains constant the antidetonating quality is improved as methyl groups in the form of side-chains are introduced. For a given number of carbon atoms in the molecule the antiknock quality is improved as centralization of the molecule is increased.[98]

Oxidation products, such as peroxides, acids, aldehydes or ketones, formed during the storage of cracked gasoline (see chapter 40), decrease the antiknock value of the fuel.[99] Accelerated oxidation of the fuel also has the same effect. The degree to which these changes take place varies with different gasolines. Oxidation of gasoline can be prevented by the use of chemical oxidation inhibitors, such as aniline, dimethylaniline, quinol, urea and anthracene. The antiknock value of stored gasolines can be increased by treating them with fuller's earth, caustic soda or borax. It has been stated that the accelerated oxidation test for gum is also applicable as an accelerated test for the depreciation of the antiknock value of a gasoline.[100]

MEASUREMENT OF KNOCK RATING

Although a detailed discussion of the various methods of determining the knock rating, or antidetonating value, of different fuels is outside the scope of this text, nevertheless, certain phases of the testing are briefly considered.

In the bouncing-pin method, which is the basis of most methods of measuring the knock rating, the relative intensities of different detonations are determined by means of a bouncing pin combined with the standard pressure element of the Midgley indicator[101] which is screwed into the combustion chamber of the engine.[102] On detonation, the pin jumps upward, the fluctuations closing an electric circuit. The volume of gas evolved from an electrolytic cell measures the period during which the circuit was closed. Comparison of these volumes determines the relative knocking values of the fuels. Hexane at one time was suggested as a standard fuel.[103] This fuel was matched in knocking tendency with the fuel under investigation by the addition of either isopropyl nitrite (knock-inducer) or diethyl selenium (knock-suppressor). Later, Faragher and Hubner[104] suggested determining the knock rating by comparing the fuel with blends of chemically pure benzene in a standard straight-run gasoline.

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[95] James, *J. Franklin Institute*, 1923, **195**, 42B.

[96] *Pet. Times*, March 7, 1931, 327. See also Meyer, German Patent 520,011, 1926; British Patent 262,363, 1925; *Brit. Chem. Abs.* **B**, 1927, 134; British Patent 269,222, 1925; *Brit. Chem. Abs.* **B**, 1927, 721; U. S. Patent 1,671,158, May 29, 1928.

[97] *Petroleum Z.*, 1926, **22**, 1344; *Chem. Abs.*, 1928, **22**, 1034.

[98] Boyd, *Oil and Gas J.*, 1931, **29** (42), 147, 227; *Chem. Abs.*, 1931, **25**, 5278.

[99] Egloff, Faragher and Morrell, *Petroleum*, 1930, **26**, 243; *Brit. Chem. Abs.* **B**, 1930, 750; also *Amer. Pet. Inst., Proc. 10th Annual Meeting*, 1930, 11, No. 1, Sect. III, 112; *Chem. Abs.*, 1930, **24**, 1967; Cassar, *Ind. Eng. Chem.*, 1931, **23**, 1132.

[100] See Chapter 40 for a discussion of the accelerated oxidation test for gum in gasoline.

[101] Midgley, *Trans. Soc. Automotive Eng.*, 1920, **15**, 317.

[102] Midgley and Boyd, *J. Soc. Automotive Eng.*, 1922, **10**, 7; *Chem. Abs.*, 1922, **16**, 815.

[103] For a comparison of the antiknocking qualities of benzene, toluene and xylene, see Midgley and Boyd, *Ind. Eng. Chem.*, 1922, **14**, 589.

Lovell, Campbell and Boyd[105] measured the knock rating of a number of paraffin hydrocarbons in terms of the aniline equivalent. This was defined as the number of centigram-moles of aniline that must be added to a reference fuel to make 1000 cc. of a fuel equivalent in knocking tendency to a molal solution of the hydrocarbon in the reference gasoline, provided the hydrocarbon knocked less than the reference fuel. When the hydrocarbon knocked more than the reference fuel the aniline equivalent was the number of centigram-moles of aniline added to a one-molal solution of the hydrocarbon in the reference gasoline to make a fuel that was equivalent in knocking tendency to the reference gasoline. On this basis n-heptane (hydrocarbon with high knocking tendency) had an aniline equivalent of —14, and 2,2,4-trimethylpentane (hydrocarbon of low knocking tendency) had an aniline equivalent of +17.

From the measurements so obtained it was found that as the length of the chain increased the knocking tendency of the hydrocarbon increased. The knocking tendency decreased as methyl groups were added as side-chains. Substances with the most compact structures were the most resistant to knocking. This is illustrated by the data in Table 155:

TABLE 155.—*Effect of Structure on Resistance to Knocking.*

Hydrocarbon	Aniline Equivalent	Hydrocarbon	Aniline Equivalent
n-Pentane	1	2-Methylbutane	9
n-Hexane	6	2-Methylpentane	4
n-Heptane	—14	2-Methylhexane	0
n-Octane	—21	2,2-Dimethylpentane	6
n-Nonane	—28	2,3-Dimethylpentane	12
n-Heptane	—14	3,3-Dimethylpentane	13
2-Methylhexane	0	2,2,3-Trimethylbutane	19
3-Methylhexane	3		

Still another method of measuring knock rating is that of comparing the knocking tendency of the fuel with various mixtures of an isooctane (2,2,4-trimethylpentane) and n-heptane. The former is a hydrocarbon which has a very slight tendency to knock, but the latter has a great tendency to knock (cf. aniline equivalents given above). The octane number of a fuel, therefore, is the percentage by volume of this isooctane in a mixture of isooctane and n-heptane required to match the knocking tendency of the fuel.[106] The higher the octane number the greater the antiknocking property of the fuel.

These primary standards, isooctane and n-heptane, are rather expensive. Alternate methods, therefore, involve the use of secondary standards such as benzene, lead tetraethyl or aniline in standard fuels, which have been rated against the primary standards.[107]

The possibility of removing from a gasoline the fraction responsible for its greatest tendency to knock was investigated by Fenske.[108] Straight-run Pennsylvania gasoline, which boiled from 43° C. to 204° C., was fractionated into 165 different fractions, of which the density, index of refraction and knock rating were determined. Unexpected periodic relations were found between the properties tested. In general, the fractions which had the lowest densities and refractive indices were found to have the highest knock ratings, and *vice versa.* Since the index of refraction, which is an easily measured constant, increased with decreasing knock rating, it was suggested that this determination be used for the separation and detection of fractions of different values.

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[104] *J. Soc. Automotive Eng.*, 1927, **20**, 405; *Chem. Abs.*, 1927, **21**, 2790.

[105] *Ind. Eng. Chem.*, 1931, **23**, 26.

[106] Boyd, *Ind. Eng. Chem.*, 1930, **22**, 1301. For the octane numbers of gasolines sold in the United States, see Kraemer and Lane, *U. S. Bur. Mines, Rep. Investigation*, **3092**; *Chem. Abs.*, 1931, **25**, 2841.

[107] Edgar, *Oil and Gas J.*, 1931, **29** (42), 101, 229; *Chem. Abs.*, 1931, **25**, 5011.

[108] *Ind. Eng. Chem.*, 1930, **22**, 913.

The variation in knock rating with the distillation range was studied by Weld.[109] A naphtha, obtained by the liquid phase cracking of a Mid-Continent gas oil, was separated by distillation into the following seven fractions: 0-10%, 10-19.1%, 19.1-28.2%, 28.2-75.1%, 75.1-81.1%, 81.1-93%, and 93-100%. These fractions were combined to form 16 different experimental gasolines, and the knock rating of each was determined. The octane number of the original gasoline (fractions 0-100%) was 55. Discarding 24.9 per cent from the heavy ends (i.e., using fractions 0-75.1%) raised the octane number 6 points, but discarding 28.2 per cent of the lighter ends (i.e., using fractions 28.2-100%) decreased the octane number by about 5 points.

In testing various fuels in Diesel engines Le Mesurier and Stansfield[110] observed that "combustion shocks" depended not only on the initial rate of pressure rise but also upon the period during which the highest rate of pressure was applied. In general, fuels having the longer period between ignition and commencement of pressure[111] produced the greatest combustion knocks. The addition of amyl nitrite (knock-inducer) or acetaldehyde reduced the angle of delay and induced smoothness of running. It also appeared that the heavy fractions of crude oils, which yielded explosion engine fuels of the highest antiknock value, would be the worst from the standpoint of combustion shocks, and *vice versa.*

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[109] *Oil and Gas J.*, March 5, 1931, p. 98.

[110] *J. Inst. Pet. Tech.*, 1931, 17, 387; *Chem. Abs.*, 1931, **25**, 5279.

[111] The use of nitroparaffins in Diesel fuels has been described by Loomis, U. S. Patent 1,820,983, Sept. 1, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1932, 636.

Chapter 45

Miscellaneous Oxidation Reactions. Denaturants, Insecticides, and Other Products

In a number of the preceding chapters the oxidation of individual hydrocarbons or of petroleum fractions has been considered. The products obtained by such reactions are principally ketones, alcohols, esters, aldehydes and various types of aliphatic and aromatic acids and anhydrides. The effect of autoxidation on certain distillates, particularly gasoline and lubricating or transformer oils has been pointed out. In this chapter are included the production of other compounds, such as alcohols, by oxidation and the utilization of these oxidized bodies in the preparation of many different kinds of materials; e.g., denaturants, insecticides, solvents, synthetic resins and waxes, plastics, detergents and emulsifying agents.

Mild or limited oxidation is sometimes employed in the refining of hydrocarbon distillates, particularly when it is desired to eliminate constituents which are readily polymerized. or resinified. In some instances sulphur compounds, present as impurities, may be preferentially oxidized to sulphur dioxide, or sulphur, and the oxides of carbon and thus be removed. A brief review of such methods is also included.

OXIDATION AS A REFINING PROCESS

For decolorizing and deodorizing naphtha, cracked oils or petroleum, an oxidation process was suggested[1] in which air is passed through a series of tanks containing the oil. The oil in the first tank may contain dissolved heavy-metal salts of fatty, naphthenic or resin acids, which are said to activate the oxygen passing to the subsequent tanks of oil containing copper or lead turnings. After oxidation, the product may be treated with acid and alkali.

Polymerization of the resin-forming constituents of oils is accelerated by treating the hot oil, or its vapors, with very small quantities of oxygen, and the polymerization products are then removed.[2] This polymerization may be further accelerated by the use of a glow discharge, irradiation, or the addition of small amounts of acids or alkalies.

The phenol fractions, boiling up to 230° C., from lignite-tar creosote can be refined by oxidation under pressure.[3] By the same procedure the liquid tar products containing a high percentage of creosote are converted into a solid condensation product which possesses electrical insulating properties.

In refining crude aromatic hydrocarbons such as benzene, toluene and naphthalene, it has been proposed to mix them in the vapor phase with air and pass them over metallic oxide catalysts. Very short periods of contact (0.25 second) are maintained. Substances such as thiophene or carbon disulphide are oxidized to sulphur dioxide, carbon monoxide and dioxide, and water, while only a small proportion of the aromatic hydrocarbon is oxidized.[4]

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[1] Petroff, British Patent 289,561, 1927; *Chem. Abs.*, 1929, **23**, 697.
[2] Tauss, German Patent 475,277, 1923; *Chem. Abs.*, 1929, **23**, 3340.
[3] Karpati, *Chem. Runds. Mitteleuropa u. Balkan*, 1926, **3**, 3; *Chem. Abs.*, 1926, **20**, 3227.

In some refining operations ozonized air is employed. For example, Bruzac[5] treated crude benzol with air having 1 per cent ozone. During treatment the benzol darkens in color and a brown precipitate settles out. After treatment, the benzol is washed with sodium carbonate solution which leaves it yellow and of sweet odor. A colorless product is obtained by distillation. The losses from this process are much less than in the usual sulphuric acid-soda treatment. This method is said to be applicable also to the light fractions from the low-temperature distillation of coal, oil shale[6] or peat. Deodorization and desulphurization are accomplished with a minimum loss, and gum- and resin-forming constituents are removed without destroying antiknock compounds. The viscosity of lubricating oils can also be increased by the procedure.

A similar process consists in subjecting the crude hydrocarbons to ozonized air followed by treatment with 70 per cent sulphuric acid, containing ferric chloride or sulphate, and washing with alkali.[6a]

The removal of easily oxidizable constituents from oil or tar products is said to be accomplished by treatment with ozone in the presence of inorganic adsorbents, e.g., silica gel or iron oxide, mixed with a base such as calcium oxide.[7] Organic acids may be recovered from the adsorbing material by subsequent treatment with steam.

Oxidation is used for refining not only liquid and solid but also gaseous hydrocarbons. For example, gases can be largely freed of their sulphur compounds by heating in the presence of metallic catalysts with sufficient oxygen to oxidize these compounds.[8] One catalyst suggested for this purpose is prepared by igniting coke impregnated with a concentrated solution of nickel nitrate. The sulphur dioxide or trioxide formed during oxidation is removed by ammonia.

Preferential catalytic oxidation is also applicable to the removal of hydrogen sulphide in fuel gas, this substance being converted to water and elemental sulphur.[9]

For the removal of any oxygen present in natural gas, the latter can be mixed with a small quantity of air and passed over porous refractory materials at 800° C. or higher. The gaseous mixture, which then contains carbon monoxide and hydrogen (substances more reactive toward oxygen than saturated hydrocarbons), is mixed with a fresh quantity of natural gas and the resulting mixture is passed over a metallic catalyst (iron or copper) at 400° to 500° C. In this latter step the oxygen present in the natural gas reacts with the carbon monoxide and hydrogen and its removal is thus effected.[10] Any hydrogen sulphide present in the natural gas is also removed in this process.

Clear purified hydrocarbon products are said to be obtained by treatment with oxidizing gases in the presence of small proportions of mineral acids, acid salts or organic acids.[10a]

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[4] Downs, U. S. Patent 1,590,965, June 29, 1926; assigned to Barrett Co.; *Chem. Abs.*, 1926, **20**, 3015.

[5] French Patent 684,618, 1929; *Chem. Abs.*, 1930, **24**, 5305; *Petroleum Times*, Aug. 16, 1930, 259.

[6] For the removal of gum-forming constituents from shale gasoline with ozone, see Baxter, *Ind. Eng. Chem.*, 1929, 21, 1096. See also Chapter 36.

[6a] Improved Hydrocarbon Processes, Ltd., British Patent 387,447, 1931; *Chem. Abs.*, 1933, **27**, 4662.

[7] Siemens and Halske A.-G., British Patent 263,186, 1926; *Brit. Chem. Abs.* **B**, 1927, 695.

[8] Wietzel, Jannek and Fried, German Patent 476,286, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1929, **23**, 3797.

[9] Furness, *J.S.C.I.*, 1923, **42**, 358.

[10] Porter, U. S. Patent 1,787,795, Jan. 6, 1931; assigned to Kay County Gas Co.; *Chem. Abs.*, 1931, **25**, 801.

[10a] I. G. Farbenindustrie A.-G., French Patent 677,200, 1929; *Chem. Abs.*, 1930, **24**, 3021.

ALCOHOLS

Methanol and other organic compounds have been prepared synthetically from carbon monoxide, or dioxide, and hydrogen. It is not within the province of this book to discuss such reactions in detail but rather from the standpoint of the use of petroleum hydrocarbons in these operations.

In one process [11] coal-gas, coke-oven gas, natural gas or cracking gas is partially oxidized with a limited quantity of oxygen to convert part or all of the hydrocarbons to carbon monoxide and hydrogen. The sulphur compounds are then removed, after which the carbon monoxide and hydrogen are caused to react, under pressure and at high temperatures, in the presence of a catalyst to yield methanol.

In producing methyl alcohol from methane Patart [12] first made carbon monoxide and hydrogen by passing methane mixed with half its volume of oxygen over coke or other combustible fuel at 800° to 1000° C. The gaseous product, which consists of approximately two volumes of hydrogen and one volume of carbon monoxide, is then converted to methyl alcohol at high temperatures and pressure in the presence of a catalyst (zinc and chromium oxides). The methane which is formed as a by-product of the last reaction is used over again in the process. Webster and Schuler [13] inject a mixture of natural gas, e.g., methane, and steam into a retort at 260° C. and the resulting mixture of carbon monoxide and hydrogen was then passed at 325° to 475° C. through a catalyst chamber. The mixture of alcohol and hydrocarbon vapors was led through a condenser which separated the alcohol and the hydrocarbons were returned to the system.

The direct production of methyl alcohol from methane has been reported.[14] The process is the same as that employed in making formaldehyde (see Chapter 38) except the gases are conducted through the reaction tube at a slower rate. The presence of hydrogen and 20 to 30 per cent of alcohol vapor in the gaseous mixture aids the reaction which appears to be the direct oxidation of methane by carbon dioxide:

$$CH_4 + CO_2 \longrightarrow CH_3OH + CO$$

In the process developed by Futacchi,[15] oxidation is carried out by treating the material either in the liquid phase or dissolved in an inert solvent. The temperatures during oxidation should not exceed 500° C., though the pressure may vary from 1800 to 9600 pounds per square inch. Catalysts such as iron, copper or vanadium may be used. Methyl alcohol and air when heated together at 180° C. and under 3000 lbs. pressure are said to yield about 40 per cent glycol, 5 per cent methyl alcohol, 20 per cent glycerol, and a viscous mixture of various carbohydrates.

Pichler and Reder [15a] observed that the best yields of methanol by oxidation of methane and ethylene are obtained by the use of high pressures and repeated combustion with small amounts of oxygen. With a mixture of methane or ethylene containing 10 per cent of oxygen, 7 per cent of the theoretical yield results, but with a mixture containing only 0.6 per cent of oxygen the methane conversion is 60 per cent. The yield of methanol was decreased by copper, nickel or cobalt oxide catalysts and increased by the presence of water vapor and carbon monoxide. The optimum temperature for methane is 350° C. With ethylene, increasing yields are obtained with rising temperatures. Sand has been suggested as a catalyst in similar reactions.[15b]

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[11] Badische Anilin- und Soda-Fabrik, British Patent 266,410, 1925; *Brit. Chem. Abs.* **B**, 1927, 316.

[12] U. S. Patent 1,836,085, Dec. 15, 1931; *Chem. Abs.*, 1932, **26**, 999; French Patent 593,650, 1925; *Brit. Chem. Abs.* **B**, 1927, 346.

[13] U. S. Patent 1,711,913, May 7, 1929; *Chem. Abs.*, 1929, **23**, 3333.

[14] H. O. Traun's Forschungslaboratorium G.m.b.H., British Patent 156,148, 1920; *J.S.C.I.*, 1922, 41, 438A.

[15] British Patent 309,498, 1929; *Chem. Abs.*, 1930, **24**, 624.

[15a] *Angew. Chem.*, 1933, **46**, 161; *Brit. Chem. Abs.* **B**, 1933, 378.

Pugh, Tauch and Warren[15c] suggested the production of alcohols by dissolving an oxidizing gas in a hydrocarbon, such as propane, butane, naphtha or gas oil in the liquid state, and passing this mixture through a reaction zone at 200°-600° C. at a pressure of 1000 to 3500 pounds per square inch. Naiman and Leggett[15d] proposed to introduce a gaseous mixture containing free oxygen and saturated aliphatic hydrocarbons over copper gauze or granulated zinc at 165° C. under a pressure of 1500 pounds per square inch. Another process consists in passing a cooled mixture of oxygen and hydrocarbons (from methane up to hexane) into a reaction zone and forcing heated hydrocarbon gases into the zone to raise the temperature.[15e] Metals that form carbides (iron, nickel or cobalt) may be employed as catalysts, as well as copper, borax and siliceous materials. The products consist of a mixture of lower aliphatic alcohols, aldehydes, acids and ketones.

Beller and Luther[15f] prepared high molecular weight alcohols by blowing paraffin wax in the liquid phase with air at 160° C. in the presence of manganese naphthenate (see Chapter 43) and treating the resulting products (after carboxylic acids are removed by sodium hydroxide) with hydrogen at 100° to 300° C. under pressures of 10 to 300 atmospheres, in the presence of nickel or a similar hydrogenation catalyst. The alcohols can be extracted with an aqueous solution of lower alcohols or their esters.

Aliphatic or cycloaliphatic mono- or poly-carboxylic acids above five carbon atoms or their esters may be hydrogenated at 170° to 250° C. under a pressure of 40 to 400 atmospheres in the presence of hydrogenation catalysts to produce alcohols. The catalysts may consist of reduced copper chromate and silica, cobalt, cobalt and potassium oxide, cobalt with 2 per cent of vanadium pentoxide or reduced cobalt carbonate and copper carbonate. Oxidized paraffin wax, ethyl oleate, palmitic and stearic anhydrides and olive oil may be thus treated.[15g]

Alcohols of high molecular weight may also be produced by oxidizing hydrocarbons of boiling point above 180° C. in the liquid phase with air containing 2 per cent or more of formic, acetic or propionic, or weak inorganic acids, until the saponification value reaches 70, in the presence of manganese naphthenate. By blowing paraffin wax at 180° C. for 3 hours with air containing 22 grams of acetic acid per cubic inch, for example, 40 per cent conversion to alcohols is said to be obtained.[15h]

Solid or liquid alcohols of high molecular weight[16] can be prepared by the reduction of more complex oxidized alkyl derivatives with aqueous alcoholic (ethyl) solutions of alkalies. A small portion of the product is frequently dehydrated to ethylenic hydrocarbons or to ethers. Stearic acid ketone (2 moles), aqueous sodium hydroxide (1 mole) and ethyl alcohol (2 moles) when heated together for 6 hours at 200° to 300° C. yield acetic acid and 1,8-pentatricontanol, $C_{35}H_{71}OH$, melting at 93°-94° C. The acids and other partial oxidation products of paraffin wax are converted to alcohols by this treatment.

[15b] Compagnie de Bethune, French Patent 630,680, 1926; *Brit. Chem. Abs.* **B**, 1930, 50; see also Chapter 38.

[15c] U. S. Patent 1,812,714, June 30, 1931; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1931, **25**, 4890.

[15d] U. S. Patent 1,878,170, Sept. 20, 1932; *Chem. Abs.*, 1933, **27**, 304.

[15e] Standard Oil Development Co.; British Patent 341,130, 1929; *Chem. Abs.*, 1931, **25**, 4890.

[15f] U. S. Patent 1,921,381, Aug. 8, 1933; *Chem. Abs.*, 1933, **27**, 5082; British Patent 367,003, 1930; *Chem. Abs.*, 1933, **27**, 1891; German Patent 570,952, 1933; *Chem. Abs.*, 1933, **27**, 4240; British Patent 352,537, 1930; *Brit. Chem. Abs.* **B**, 1931, 1040; all patents assigned to I. G. Farbenindustrie A.-G. *Cf.* Dietrich and Luther, German Patent 564,208, 1929; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 992.

[15g] I. G. Farbenindustrie A.-G., British Patent 356,731, 1930; *Brit. Chem. Abs.* **B**, 1932, 94.

[15h] I. G. Farbenindustrie A.-G., British Patent 353,047, 1930; *Brit. Chem. Abs.* **B**, 1931, 1132.

[16] G. Schicht A.-G., German Patent 327,510, 1916; *J.S.C.I.*, 1921, **40**, 196A.

Ethylene can be directly oxidized to either glycol or chlorhydrin.[17] For the production of the former, the ethylene is fed into a vessel in which is placed water containing some substance which aids in holding the gas in solution. These substances may be solids such as bone black, charcoal, or platinum black, or oily liquids such as turpentine. At the same time a solution of an oxidizing agent such as a permanganate or bleaching powder containing a small quantity of cobalt chloride can be added. The cobalt salt acts as a catalyst, causing the decomposition of the bleaching powder with the evolution of oxygen. If chlorhydrin is desired, bleaching powder alone is used, and a weak acid, such as boric acid, is added to liberate hypochlorous acid.[18] Instead of using bleaching powder, chlorine can be passed into the aqueous solution of ethylene in which is suspended calcium or magnesium carbonate. These carbonates neutralize the hydrochloric acid formed by the reaction between chlorine and water.

The direct electrolytic oxidation of ethylene to glycol can also be effected in solutions of salts of oxygen acids, for example, sulphates or borates. Manganese, chromium or cerium salts may also be added. During oxidation ethylene is led into the cell so as to maintain the gas and liquid in the condition of a foaming mass or emulsion. If sodium chloride is used as the electrolyte, the product first obtained is chlorhydrin. The formation of this compound, however, is accompanied by the accumulation of an equivalent quantity of alkali (from the electrolysis of the sodium chloride) and this alkali saponifies the chlorhydrin to glycol with the re-formation of sodium chloride. During the electrolytic oxidation, rises in temperature are avoided by the use of external cooling.

SOLVENTS AND MOTOR FUELS

It is best to consider solvents and motor fuels simultaneously, as they may both be made by oxidation methods which produce low-boiling hydrocarbons from high-boiling hydrocarbons. The production of motor fuels is probably dependent on the formation of unsaturated hydrocarbons, alcohols and also in some degree, esters, aldehydes, ketones, and ethers. All of these products could be formed by the direct oxidation of the hydrocarbons, or by the reactions of the oxidation products themselves (e.g., esters by the condensation of aldehydes alone, or from the alcohols and acids), and such substances are said to increase the antiknock value of the motor fuel. The solvent properties of the products are dependent on the presence of alcohols, esters, aldehydes and ketones.[18a]

In obtaining other products from the Penniman[19] process (Chapter 36), the distillate is separated into two layers, an upper layer of oil-soluble products, and a lower aqueous layer which contains water-soluble substances. The upper layer, consisting of acids, aldehydes, alcohols, unsaturated hydrocarbons and other substances, is given a light alkali treat, followed by washing with water. It is then treated with a small proportion of acid and distilled. The fraction distilling up to 204° C. (400° F.) can be used as a motor fuel, and the residue recycled. The water layer, which consists of aldehydes, ketones, alcohols and acetals, when distilled yields a fraction boiling between 45° and 85° C., which, after a mild alkali treat, can be used as a solvent in the extraction of fats, for nitrocellulose, and for gums and varnishes. It may be added also to fuels for internal combustion engines.

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[17] McElroy, U. S. Patents 1,308,796 and 1,308,797, July 8, 1919; both assigned to Chemical Development Co.; *Chem. Abs.*, 1919, 13, 2217; *cf.* U. S. Patent 1,295,339, Feb. 25, 1919; *Chem. Abs.*, 1919, 13, 1217.

[18] See Higgins, *J.C.S.*, 1913, 103, 1816; also *J. Franklin Inst.*, 1914, 177, 314.

[18a] Solvents consisting of oxygenated and halogenated hydrocarbons such as halogenated ethers, ketones, alcohols, aldehydes or acids can be used in the removal of undesirable substances from mineral oils, according to the Standard Oil Co. (French Patent 739,542, 1932; *Chem. Abs.*, 1933, 27, 2294).

[19] British Patent 252,327, 1925; British Patent 255,020, 1925. *Cf.* U. S. Patent 1,894,097, Jan. 10, 1933; *Chem. Abs.*, 1933, 27, 2227; U. S. Patent 1,907,822, May 9, 1933; *Chem. Abs.*, 1933, 27, 3761; U. S. Patent 1,894,352, Jan. 17, 1933; *Chem. Abs.*, 1933, 27, 2570.

The lower-boiling fractions of the condensate obtained in the vapor-phase catalytic oxidation of high-boiling hydrocarbons have been suggested as solvents. The acids present in the oxidation product may be esterified by heating with alcohols and the resulting esters can be separated by distillation.[20] The fractions which boil between 100° and 250° C. have been proposed as solvents for nitrocellulose or varnish gums in the preparation of lacquers. If aldehydes and ketones only are desired they can be obtained by extraction of the oxidation product with solutions of sodium bisulphite. Instead of distilling the oxidation products they may be extracted with an immiscible solvent, e.g., 50 per cent alcohol, and the solvent subsequently separated by distillation.

For producing motor fuels and other products, Ellis[21] allowed a petroleum distillate such as kerosene to run slowly into a reaction chamber containing a catalyst supported on pumice and kept at a temperature of 430° to 450° C. while air is forced into the reaction chamber. The exit gases are then condensed. This condensate is a gasoline substitute. Acids and aldehydes can be removed from it by scrubbing with water. This process may also be modified by first passing the kerosene through a cracking tube kept at 540° to 590° C., then through a trap to remove easily condensible substances and subsequently through a reaction chamber which contains a catalyst. Moist air is passed into the reaction chamber at the same time. A gasoline substitute, together with acids, is again obtained. Catalysts such as copper, chromium or vanadium oxides or duplex catalysts such as iron vanadate or silver chromate can be used.

In a method for producing motor fuel, the vapors of the heavier hydrocarbons together with air are passed through screens containing catalysts such as the oxides of molybdenum, vanadium, or uranium.[22] The lighter fractions of the oxidation product, boiling up to 200° C., are separated by distillation and used as motor fuels. The heavier fractions are recycled. Any free acids in the products are eliminated by distillation over sodium hydroxide. In place of air, steam may be used, and the hydrocarbon vapor and steam are passed over metallic catalysts at a temperature of about 450° C. The metal is oxidized by the steam to give hydrogen and the metallic oxide.

Heavy petroleum hydrocarbons, such as heavy lubricating oils or wax distillates, are first mixed with light petroleum and the mixture is vaporized with steam.[23] This mixture of vapors can then be passed through a series of catalytic screens without clogging. The high molecular weight hydrocarbons are preferentially oxidized. The best results are obtained when only a portion of the required air is put into the vaporizing chamber, and the remainder added after the mixture has passed the first screen.

Strache and Porges[24] passed the vapors of the hydrocarbons mixed with steam over a catalyst such as iron or lead oxide or manganese dioxide at 600° C. This process, however, is not a continuous one since the metallic oxide, which is the actual oxidizing agent, must be regenerated from time to time.

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[20] James, U. S. Patents 1,782,963 and 1,782,964, Nov. 25, 1930; British Patent 259,293, 1925; *Chem. Abs.*, 1927, 21, 3473.

[21] U. S. Patent 1,697,263, Jan. 1, 1929; assigned to Ellis-Foster Co. Other processes for the oxidation of petroleum distillates developed by Ellis are described in Chapter 36.

[22] James, U. S. Patent 1,597,796, Aug. 31, 1926; *Brit. Chem. Abs.* **B**, 1926, 972. James, U. S. Patent 1,597,798, Aug. 31, 1926; *Brit. Chem. Abs.* **B**, 1926, 973. British Patent 209,128, 1924; *Chem. Abs.*, 1924, 18, 1565.

[23] James, U. S. Patent 1,597,797, Aug. 31, 1926; *Brit. Chem. Abs.* **B**, 1926, 972.

[24] U. S. Patent 1,205,578, Nov. 21, 1916; *Chem. Abs.*, 1917, 11, 207; British Patent 1,329, 1915; *Chem. Abs.*, 1916, 10, 1926.

Reid[25] produced low molecular weight hydrocarbons, which boil within the gasoline range, by the oxidation of petroleum distillates at 300° to 500° C. under 300 pounds per square inch pressure. The air, which is the oxidizing agent, is disseminated throughout the liquid in an extreme degree of subdivision, comparable to molecular dispersion. In this way the rate of oxidation is very greatly increased. This subdivision of the air can be obtained with a very rapidly rotating stirrer (for example, a Witt stirrer). The gasoline vapors are continuously withdrawn and condensed during the process of oxidation. By lowering the temperature of oxidation it is possible to obtain partially oxidized products such as aldehydes.

Beall[25a] prepared a motor fuel composed of a partially oxidized liquid hydrocarbon mixture. Natural gas and an oxygen-containing gas are compressed and heated separately. The two gases (without previous mixing) are passed under pressure through a reaction zone over a platinum catalyst, under such conditions of time and temperature that a liquid, partially oxidized mixture results.

The deposition of carbon during the cracking of high molecular hydrocarbons is said to be largely avoided by a method developed by the I. G. Farbenindustrie A.-G.[26] A liquid hydrocarbon is heated by rods or wire of metals, graphite, or silicon carbide. These rods are placed in the liquid and heated electrically to the desired temperature while they are exposed to a blast of air, hydrogen, steam or ammonia. If the cracking temperature is maintained at 500° C. the product is principally an oil boiling between 80° and 300° C. and the gases are mainly olefins. At higher temperatures (700° to 1000° C.) the product is an oil of lower boiling range together with a gas that is principally methane.

Low-boiling hydrocarbons can also be obtained by distillation of heavy hydrocarbons in the presence of oxidizing agents such as potassium permanganate or dichromate, or manganese dioxide.[27] This process is applicable to such materials as resins, pitch, waxes, tars and asphalts. The reaction may be assisted by ionizing the vapors by means of high-frequency discharges.

Howard[28] produced motor fuels of high antiknock value by passing a mixture of the higher-boiling fractions of gasoline and air (in the proportion of 4 mols. of oxygen to 1 mol. of the hydrocarbon) through tubes heated to 230° to 370° C. The condensed products are steam-distilled to remove gummy substances, and can then be blended with other gasolines. In a procedure which has been developed by Hopkins,[29] the vapors obtained by the distillation of high-boiling fractions, such as kerosene, are mixed with air and passed through a heating zone kept below the cracking temperature (385° to 470° C) (725° to 875° F.). The gaseous mixture, after passing through a rectifying column, is washed with sodium hydroxide solution and distilled. This process seems to be principally dehydrogenation, as the acid adsorption value of product indicates a high percentage of unsaturated hydrocarbons.

Stryker[29a] suggested adding about 0.2 to 1 per cent of a completely soluble oxidized paraffin wax to gasoline or kerosene, the oxidized wax serving as a lubricant in the cylinders of internal-combustion engines.

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[25] U. S. Patent 1,663,523, Mar. 20, 1928; assigned to E. I. duPont de Nemours & Co., Inc.

[25a] U. S. Patent 1,859,193, May 17, 1932; *Chem. Abs.*, 1932, **26**, 3904.

[26] British Patent 295,974, 1927; *Brit. Chem. Abs.* **B**, 1928, 806.

[27] Girard, Petit and Charbonneau, British Patent 299,861, 1927; *Chem. Abs.*, 1929, **23**, 3563. The production of liquid fuels by nitration has also been suggested (Charbonneau, U. S. Patent 1,480,372, Jan. 8, 1924, and Chapter 47).

[28] U. S. Patent 1,758,898, May 13, 1930; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 11.

[29] U. S. Patent 1,767,363, June 24, 1930; assigned to Standard Oil Development Co.

[29a] U. S. Patent 1,826,439, Oct. 6, 1931; assigned to Texas Co.; *Brit. Chem. Abs.* **B**, 1932, 715.

Watkins [29b] prepared a gas for heating purposes by passing heated air through a conduit under superatmospheric pressure, the heat from the air being used to partially vaporize liquid hydrocarbons, which were then mixed with the air.

EMULSIFYING AGENTS

Emulsifying agents can be prepared from the oxidation products of petroleum, particularly from paraffin wax. As shown in Chapter 43, the oxidation of these solid hydrocarbons leads to the production of wax acids of high molecular weight together with saponifiable material, most probably esters. These products can then be treated with alkalies, either before or after the removal of the acids, and the resulting soaps can be used for making emulsions of many different types. This is apparently the basis for most of the processes, which differ only in the manner in which the various steps are carried out.

For example, the oxidation products of solid paraffin are treated with a quantity of alkali hydroxide just sufficient to saponify the saponifiable constituents.[30] Hydrocarbons, or other liquids which are insoluble in water and which may contain sulphur or other dissolved substances, can be added before or after saponification. The product so formed can be used either as an emulsifying agent for drilling oil and other similar oils, or directly as a lubricating oil.

Partially oxidized wax, or mixtures of petroleum and other waxes (also partially oxidized), has also been proposed as an ingredient for paper sizes by Ellis.[31] For low grades of paper, where color is not important, the blown or oxidized wax can be mixed with various petroleum distillates. For high-grade paper a white oil such as "Nujol" or "Marcol" is employed. The sizing is made by dispersing the oil and oxidized wax mixture in an aqueous medium with emulsifying agents such as soap or silicate of soda. Other sizing agents, such as rosin, can also be used along with the blown wax.

The oxidation products of paraffin wax have been mentioned as stabilizers for asphalt emulsions.[32] The wax is oxidized by passing a rapid stream of oxygen through it at 150° to 160° C., in the presence of metallic soaps as catalyzers. The oxidation product is then dissolved to the extent of 0.1 to 0.3 per cent in petroleum asphalt (m.p. 40° C.) and the mixture is poured into an equal volume of dilute alkali solution (0.5 per cent), agitated well, and heated to 90° to 100° C.

In another process [33] the wax is oxidized until the acidic contents amount to about 30 per cent by weight. The oxidation is carried out at 160° C., under pressure, and in the presence of catalysts such as manganese oleate. The oxidized material is then washed and pressed to remove the highly acidic substances. The resulting products are subsequently neutralized with alkali and emulsified with water. An emulsion is obtained which has been suggested for use as a textile dressing, and also for the "proofing" of permeable materials such as strawboard, asbestos, brick, stone, or concrete. The addition of rosin or other size to the oxidized product before neutralization yields an emulsion which can be used in sizing paper.

[29b] U. S. Patent 1,903,583, April 11, 1933; assigned to Skelly Oil Co.; *Chem. Abs.*, 1933, **27**, 3321.

[30] Pungs and Luther, German Patent 438,180, 1922; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* B, 1927, 548.

[31] Ellis, U. S. Patent 1,739,580, Dec. 17, 1929; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1930, **24**, 965.

[32] Bataafsche Petroleum Maatschappij, Dutch Patent 14,751, 1926; *Chem. Abs.*, 1926, **20**, 3077.

[33] Burwell, U. S. Patent 1,768,523, June 24, 1930; British Patent 287,514, 1927; *Chem. Abs.*, 1929, **23**, 510; U. S. Patent 1,791,860, Feb. 10, 1931; *Chem. Abs.*, 1931, **25**, 1997; German Patent 570,798, 1933; *Chem. Abs.*, 1933, **27**, 4400; all patents assigned to Alox Chemical Corp. Luther and Beller, German Patent 566,797, 1930; addn. to German Patent 438,180, 1922; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2542.

Beller and Pfaff[83a] prepared an emulsifying agent by treating high molecular weight hydrocarbons, or a partially oxidized mixture containing about 70 per cent or more of unchanged hydrocarbons, with sodium carbonate and ammonium stearate.

Hydroxyalkyl ethers of aliphatic polyhydric alcohols containing more than 2 carbon atoms may be etherified or esterified with aliphatic compounds containing more than 5 carbon atoms, of which at least 2 hydroxyls are left free, to obtain wetting, cleansing and dispersing agents. Such compounds are sorbitol hexa-(2-hydroxyethyl) ether with lauric acid, linoleic acid, coconut oil acids, or acids containing from 8 to 11 carbon atoms from oxidized paraffin wax.[83b]

PAINT VEHICLES AND DRIERS

In one process, paint vehicles are made by hydrogenation followed by oxidation of a mineral oil. This product is then mixed with drying, semi-drying or non-drying oils. Only mild oxidation need be applied. For example, the mineral oil is heated in contact with manganous oxide at 85° to 90° C. (185° to 194° F.) for about two hours.[84] Tung oil may be added to the final blend.

Driers are obtained by treating the crude or saponifiable oxidation products of paraffin or montan wax with the oxides or salts of the alkaline earths or metals such as aluminum, zinc, manganese or lead to form products which are insoluble or only slightly soluble in water.[85] These products may be used alone or mixed with salts of high molecular weight acids of natural origin, e.g., resinates, linoleates, or stearates.

Mixtures of aluminum resinates obtained from petroleum distillates and low-boiling petroleum fractions have been proposed as substitutes for linseed oil.[86] The aluminum compounds are prepared in the following manner: The sodium soaps obtained from the alkali used in washing acid-treated lubricating oils are dissolved in a light hydrocarbon, dilute sulphuric acid is added to neutrality, followed by the addition of a dilute solution of aluminum sulphate. The solution of aluminum resinate so obtained is separated, the solvent is removed, and the residue is then ready to mix with a low-boiling hydrocarbon.

Metallic salts of acids of oxidized mineral oils dissolved in low-boiling petroleum fractions, aromatic hydrocarbons or terpenes have been suggested as varnishes by Petrov, Danilovich, and Rabinovich.[86a]

Compositions which may be used as weather-proof coatings for stone-work have been made by mixing drying oils with higher aliphatic alcohols, the latter having been prepared by the oxidation of paraffin hydrocarbons or by catalytic reduction of the acids of paraffin hydrocarbons.[86b] Any acids present in such oxidation products may be converted into aluminum or zinc salts and added in this form. Varnish products with a high luster have been prepared by heating the alcohol obtained from oxidized paraffin wax with turpentine and ozokerite, or with nigrosin to produce a shoe polish.[36c] Fatty acids of oxidized paraffins, montan or carnauba wax mixed with turpentine or similar substances and then emulsified with water by means of soaps or sulphonic acids have been proposed as polishing materials.[36d]

[83a] German Patent 564,922, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 1115.

[83b] I. G. Farbenindustrie A.-G., British Patent 375,842, 1931; *Brit. Chem. Abs.* B, 1932, 973; *cf.* British Patent 380,431, 1931; *Brit. Chem. Abs.* B, 1932, 1114.

[84] Blakeman, U. S. Patents 1,385,033, 1,385,034, 1,385,035, 1,385,036, 1,385,037, July 19, 1921; *J.S.C.I.*, 1921, 40, 667A; U. S. Patent 1,423,390, July 18, 1922; *Chem. Abs.*, 1922, 16, 3218; U. S. Patents 1,430,881 and 1,430,882, Oct. 3, 1922; *Chem. Abs.*, 1922, 16, 4073.

[85] I. G. Farbenindustrie A.-G.; British Patent 311,716, 1928; *Chem. Abs.*, 1930, 24, 979.

[86] Maitland, U. S. Patent 1,425,882, Aug. 15, 1922; *J.S.C.I.*, 1922, 41, 741A; U. S. Patent 1,528,884, Mar. 10, 1925; *J.S.C.I.*, 1925, 44, 514B; both patents assigned to Sun Oil Co.

[86a] Russian Patent 23,511, 1931; *Chem. Abs.*, 1932, 26, 2071. The properties of these varnishes of Petrov have been investigated by Vedenkin, *Malyarnoe Delo*, 1931, No. 3, 26; *Chem. Zentr.*, 1931, 2, 2793; *Chem. Abs.*, 1932, 26, 5219.

[86b] I. G. Farbenindustrie A.-G., British Patent 375,002, 1931; *Brit. Chem. Abs.* B, 1932, 807.

Weber[36e] prepared a coating composition by dissolving nitrocellulose in a water-soluble, acetylated oxygenated petroleum derivative boiling between 66° and 85° C., with an acetylated distillate from the volatile water-soluble petroleum oxidation products boiling between 77° and 95° C., and adding this mixture to a solution containing rosin-phthalic glyceride resin. Cellulose acetate or other cellulose esters or ethers and other synthetic resins, such as benzoic phthalic glyceride, salicylic phthalic glyceride, or natural resins may be used similarly.

Lubricants and Greases

Penniman[37] obtained machine lubricants by adding to a hydrocarbon of low viscosity, (1) a "polar body," such as oleic acid, or the higher alcohols and ketones obtained by oxidizing petroleum with air, (2) a protective material, e.g., a mixture of castor oil and oleic acid, and (3) an antioxidant, lead tetraethyl and phenyl disulphide being examples.

James[38] oxidized petroleum distillates to obtain a large percentage of aldehydes and alcohols and condensed these to form acetals which may be used as lubricants. Condensation is also accompanied by some polymerization of the aldehydes, which is said to result in the formation of lubricating bodies. Alternatively, the petroleum may be oxidized to give a large quantity of aldehyde acids. This product can be mixed with one containing a larger quantity of alcohols to obtain liquid mineral waxes or esters, which also are proposed as lubricants.

Dengler[38a] manufactured lubricants by oxidizing, with air at 205° to 270° C., the residues of paraffin or semi-paraffin crudes having flash points of 190° to 245° C.

The addition of small proportions (0.25 to 2.0 per cent) of oxidized paraffin wax to lubricating oils appears to enhance the lubricating power of the oils. This applies to lubricating oils for machinery cutting tools and molds,[39] lubricants for internal-combustion engines,[40] and lubricants for transmission systems of automobiles.[41] The unsaponifiable matter may be removed from the oxidized wax before using.

Greases were produced by James[42] by careful neutralization of the acids in partially oxidized petroleum with alkalies such as lime or sodium hydroxide, carbonate, or bicarbonate. Upon neutralization, the soaps formed cause an emulsification of the whole product. The grease thus obtained, either before or after blending with other oils or greases, can be brought to the desired consistency by careful evaporation of the water.

[36c] I. G. Farbenindustrie A.-G., British Patent 388,369, 1931; *Brit. Chem. Abs.* B, 1933, 436.

[36d] Henkel and Co., G.m.b.H., British Patent 381,387, 1931; *Brit. Chem. Abs.* B, 1932, 1090.

[36e] U. S. Patent 1,835,105, Dec. 8, 1931; assigned to Ellis-Foster Co.; *Chem. Abs.*, 1932, 26, 1143.

[37] British Patent 317,406, 1928; *Chem. Abs.*, 1930, 24, 2285.

[38] U. S. Patent 1,700,055, Jan. 22, 1929; *Chem. Abs.*, 1929; 23, 1262.

[38a] U. S. Patent 1,781,444, Nov. 11, 1930; assigned to Texas Co.; *Brit. Chem. Abs.* B, 1931, 619.

[39] Alox Chemical Corp., British Patent 335, 152, 1928; *Chem. Abs.*, 1931, 25, 1375; French Patent 672,813, 1928; *Chem. Abs.*, 1930, 24, 2285.

[40] MacCoull, U. S. Patent 1,767,147, June 24, 1930; assigned to Texas Co.; *Chem. Abs.*, 1930, 24, 4377.

[41] MacKenzie and Haskell, U. S. Patent 1,705,298, Mar. 12, 1929; *cf.* MacKenzie, U. S. Patent 1,904,065, April 18, 1933; *Chem. Abs.*, 1933, 27, 3326; both patents assigned to Texas Co.

[42] U. S. Patent 1,700,056, Jan. 22, 1929.

WAXES AND RESINS

As mentioned in Chapter 43, the oxidation of paraffin wax progresses through the formation of esters which are further oxidized to acids. This oxidation can be made to yield substances for the preparation of artificial waxes. Waxes produced by this method are held to be substitutes for carnauba, beeswax, and other similar substances.

Before oxidation the paraffin may be mixed with resins, and oxidation of the mixture serves as a purification step. For example, Schliemann[43] produced artificial waxes by oxidizing a mixture of paraffin and American resins or French colophony at 90° C. with air. During this operation an insoluble resin separates and the mass assumes a peculiar sweet odor. After separation of the insoluble portion the mass is cooked with steam. It can then be mixed with smaller quantities of high-melting paraffins and coloring matter. The finished paraffin-resin mixture is a plastic mass which can be kneaded without sticking and retains this property after long storage. It can be used in many technical applications as a substitute for wax or rosin.

A number of processes have been developed for the manufacture of such materials as shoe polishes, creams, and floor polishes, and substitutes for beeswax. In the production of a substitute for beeswax,[44] paraffin wax is oxidized at 150° C. with air and the oxidation product is then separated into a solid and a semi-solid portion by pressing or by extraction with organic solvents. Synthetic wax thus obtained from a paraffin wax melting at 52° C. had the following characteristics: acid value, 21; saponification value, 75.6; iodine value, 4.7.

Artificial waxes are also produced by bleaching montan wax with oxygen, or by oxidizing mixtures of paraffin wax, castor oil, and resins[45] for a short time in the presence of oxidizing catalysts. Any free acids formed can afterwards be esterified with glycol.

For the making of light colored wax-like substances which can be used as shoe or floor polishes, heated mixtures of oils and lignite wax, or other similar mixtures of vegetable or animal fats and waxes or resins are oxidized with air in the presence of contact materials such as clay, glass, aluminum rings or balls.[46]

Waxes which have similar uses are obtained by the oxidation of montan wax with a mixture of chromic and hydrochloric or phosphoric acids.[47] Too vigorous oxidation and carbonization must be prevented. The products are white or light yellow in color. The oxidized wax is then partly esterified with glycol and partly neutralized with lime. The material can be further improved by the addition of glycol esters to reduce its salt content to not more than 15 to 20 per cent.

Acetic acid may also be substituted for hydrochloric or phosphoric acid in the oxidation of montan wax.[48] The product thus obtained can be used as a substitute for beeswax, or it can be mixed with oxidation products of paraffin hydrocarbons to give wax-like materials.

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[43] British Patent 16,472, 1898; *J.S.C.I.*, 1898, **17**, 932; German Patent 101,222, 1898; *Chem. Zentr.*, 1899, 1, 864.

[44] Grün, British Patent 183,186, 1921; assigned to G. Schicht A.-G.; *J.S.C.I.*, 1922; **41**, 719A.

[45] I. G. Farbenindustrie A.-G., British Patent 320,854, 1928; *Brit. Chem. Abs.* **B**, 1930, 156.

[46] Badische Anilin and Soda Fabrik, British Patent 258,099, 1925; *Chem. Abs.*, 1927, **21**, 3138.

[47] I. G. Farbenindustrie A.-G., British Patent 296,145, 1927; *Brit. Chem. Abs.* **B**, 1928, 779; British Patent 305,552, 1927; *Brit. Chem. Abs.* **B**, 1929, 273; British Patent 315,283, 1928; *Brit. Chem. Abs.* **B**, 1929, 804. British Patent 324,631, 1928; *Brit. Chem. Abs.* **B**, 1930, 519; *cf.* British Patent 354,782, 1930; *Brit. Chem. Abs.* **B**, 1931, 962; British Patent 362,632, 1930; *Brit. Chem. Abs.* **B**, 1932, 270. The bleaching of montan wax by oxidation is described in British Patent 305,552, 1927; *Brit. Chem. Abs.* **B**, 1929, 273; British Patent 308,996, 1927; *Brit. Chem. Abs.* **B**, 1929, 425; British Patent 320,854, 1928; *Brit. Chem. Abs.* **B**, 1930, 156.

[48] Pungs, German Patent 409,420, 1922; assigned to Badische Anilin- und Soda-Fabrik; *J.S.C.I.*, 1925, **44**, 436B.

The synthesis of waxes from fatty acids, or from the wax acids resulting from the oxidation of paraffin wax, has been accomplished by Grün, Ulbrich, and Krczil.[49] The acids were converted to ketones, from which the secondary alcohols, olefins and esters found in natural waxes could be made. The mixed wax esters were much easier to prepare than the individual esters and had more useful properties. Stearic acid, for example, when heated in an iron vessel for 4 hours at 300° C. gave a 91 per cent yield of ketone. The ketone was reduced by heating with a mixture of ethyl alcohol and sodium hydroxide solution, and the secondary alcohol obtained was easily esterified with acid chlorides. After neutralization of the excess acid, the ester and salts were separated by the Hönig and Spitz method[50] with petroleum ether and 50 per cent alcohol. To accomplish further separation of the unesterified wax alcohol from the reaction product it was extracted with hot alcohol in which the esters are insoluble. High yields of waxes were obtained in this way.

Szidon[51] produced a white paraffin wax melting at 45° C. by the oxidation of spindle oil in the presence of copper oxide at 180° C. under pressure.

Hard resins which are said to be of value in the manufacture of varnishes are made by oxidizing the resinous substances removed from cracked petroleum distillates by adsorbing agents.[52] The oxidation is effected with air at slightly elevated temperatures and in the presence of polymerizing agents such as the salts of heavy metals. Resins may also be obtained by heating cracked petroleum distillates with phenolic substances, e.g., wood- or coal-tar distillates. These distillates are heated to a temperature of about 150° C. while oxidizing gases (ozone, air, or an oxide of chlorine) are passed into the mixture until the desired consistency is obtained.[53]

Ramage[54] produced an oxidized resin by treating rosin dissolved in liquid hydrocarbons with air or ozonized air at 93° C. (200° F.). The oxidized product possesses lower iodine and saponification values than the original product, though the acid value is higher, and the metallic salts of the oxidized product are much less soluble than those of the original substance. The oxidized product can be used in the manufacture of paints and varnishes, and as a filler for plastic molding.

Products containing resinous oxygen-containing substances, paraffin compounds, oily liquids, alcohols and aqueous solutions of organic acids have been obtained by passing mixtures of oxides of carbon and hydrogen over iron catalysts containing small proportions of alkalies and alkaline earths at about 200° C., under atmospheric, slightly reduced, or increased pressures.[54a]

PLASTICS AND RELATED SUBSTANCES

Products which can be used in the manufacture of linoleum, lacquers, or rubber compounds may be obtained in the following manner: The liquid acids insoluble in petroleum ether, which are obtained on the oxidation of paraffin wax, are esterified at 150° C. or above with alcohols containing at least two hydroxyl groups, such as glycol or glycerol. The alcohols may be mixed with organic unsaturated acids or hydroxy-acids, such as linoleic acid, or with their glycerides. Before or during the heating process the liquid acid portion is heated with siccatives, e.g., lead oxide, or with sulphur or sulphur compounds.[55] The same class of substances can also be obtained by using the unsaturated fatty acids made by the dehydration of the oxidation products of paraffin wax in place of the acids just mentioned.[56]

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[49] *Z. angew. Chem.*, 1926, **39**, 421; *Chem. Abs.*, 1926, **20**, 2818.

[50] See Chapter 43.

[51] French Patent 640,534, 1927; *Chem. Abs.*, 1929, **23**, 846.

[52] Morrell and Egloff, U. S. Patent 1,627,054, May 3, 1927; assigned to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1927, 635.

[53] Morrell and Egloff, U. S. Patent 1,766,927, June 24, 1930; *Brit. Chem. Abs.* **B**, 1931, 261; *cf.* U. S. Patent 1,744,135, Jan. 21, 1930; *Chem. Abs.*, 1930, **24**, 1529; both patents assigned to Universal Oil Products Co.; *cf.* I. G. Farbenindustrie A.-G., French Patent 735,906, 1932; *Chem. Abs.*, 1933, **27**, 1221.

[54] Ramage, U. S. Patent 1,752,693, April 1, 1930; *Chem. Abs.*, 1930, **24**, 2623.

[54a] I. G. Farbenindustrie A.-G., British Patent 280,522, 1926; *Chem. Abs.*, 1928, **22**, 3169.

Milvitzkii and Maksorov[56a] produced synthetic resins by heating at 180° to 220° C. a mixture of glycerol and phthalic anhydride with carboxylic acids, obtained from the oxidation of paraffin hydrocarbons. Petrov[56b] suggested the formation of resins by condensing acids obtained in the oxidation of petroleum distillates with aldehydes in the presence of amines.

It has been stated that plastic materials are produced by the reaction of alginic acid with hydrocarbons (paraffin wax), followed by the addition of an alkali, sodium hydroxide or ammonia.[57] Finely divided metals may be added to the product.

When liquid petroleum, for example, fuel oil, is oxidized at 130° to 160° C. under 150 to 350 pounds per square inch pressure in the presence of catalysts the reaction mixture eventually separates into three layers.[58] The upper and lower layers contain principally unchanged hydrocarbons, petroleum-soluble materials, and an aqueous solution of acids, respectively. The middle layer, principally hydroxy-acids insoluble in petroleum, is separated and distilled at low pressures (10 to 20 mm. of mercury) to yield artificial asphalt. The temperature of distillation varies from 140° to 275° C.; the higher the temperature, the harder and more brittle are the products obtained. The less brittle products, however, have high dielectric properties.

Hard-blown products of mixed petroleum residues or other asphaltic bitumens, with softening points of about 50° C. and penetrations between 8 and 16 at 50° C. (A.S.T.M.), are advantageous ingredients for rubber. Such materials can be prepared by blowing a mixture of 60 and 40 per cent, respectively, of residues from Illinois and California petroleums.[59] From 5 to 25 per cent of this oxidized material can be added to rubber before vulcanization.

Oxidation of petroleum distillates, of 43° to 48° Bé., in the liquid phase can be effected at 130° to 140° C. under 150 to 350 pounds per square inch pressure, so as to avoid as much as possible the production of hydroxy-acids. The acids thus obtained, after separation from aldehydes and ketones, can be used as plasticizers for coating compositions of nitrocellulose, for artificial rubber, or can be esterified to give substitutes for castor oil.[60]

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[55] Luther and Held, U. S. Patents 1,884,023 and 1,884,024, Oct. 25, 1932; *Chem. Abs.*, 1933, **27**, 1222; German Patent 575,954, 1933; *Chem. Abs.*, 1933. **27**, 4890; British Patent 322,496, 1928; *Chem. Abs.*, 1930, **24**, 2904; all patents assigned to I. G. Farbenindustrie A.-G.

[56] I. G. Farbenindustrie A.-G., British Patent 323,580, 1928; *Chem. Abs.*, 1930, **24**, 3134. French Patent 676,659, 1929; *Chem. Abs.*, 1930, **24**, 3135.

[56a] Russian Patent 27,789, 1931; *Chem. Abs.*, 1933, **27**, 2321.

[56b] Russian Patent 27,468, 1931; *Chem. Abs.*, 1933, **27**, 2321; *cf.* Russian Patent 24,585, 1931; *Chem. Abs.*, 1932, **26**, 2334.

[57] Burgess, U. S. Patent 1,782,887, Nov. 25, 1930; assigned to Plastic, Inc.; *Chem. Abs.*, 1931, **25**, 389.

[58] Alox Chemical Corp., British Patent 309.384, 1927; *Brit. Chem. Abs.* **B**, 1929, 651. See also Burwell, U. S. Patents 1,770,875 and 1,770,876, July 15, 1930; assigned to Alox Chemical Corp.; *Chem. Abs.*, 1930, **24**, 4647.

[59] Winkelmann, U. S. Patent 1,751,848, March 25, 1930; assigned to B. F. Goodrich Co.; *Brit. Chem. Abs.* **B**, 1931, 77.

[60] Alox Chemical Corp., British Patents 303,560 and 303,566, 1927; *Brit. Chem. Abs.* **B**, 1929, 219; also Burwell, Canadian Patent 283,892, 1928; assigned to Alox Chemical Corp.; *Chem. Abs.*, 1929, **23**, 704; Burwell, U. S. Patent 1,791,711, Feb. 10, 1931; assigned to Alox Chemical Corp.; *Chem. Abs.*, 1931, **25**, 2019.

SUBMERGED COMBUSTION

In the cracking of asphalts, cracking pitches or still residues, Ellis[61] used submerged combustion.[62] The process may be operated at atmospheric or increased (20 atmospheres or more) pressure. Under pressures above atmospheric, submerged combustion is more intensified and more positive. The burner is supplied with air and fuel (gaseous, liquid or solid) at such a rate as to maintain a temperature of about 425° C. (800° F.). The volatile products formed are recovered by passing them through a heat exchanger, to preheat the oil fed to the still, then through a condenser and scrubber, and subsequently through an absorber.

Submerged combustion is particularly applicable to the distillation of tar or tar oils, and to the cracking of petroleum. In some instances, the steam produced can be utilized for the generation of power.

Nitric acid and oxides of nitrogen are obtained in the combustion of oil or other fuel and air in a flame submerged in water, and in the presence of catalysts such as vanadium, nickel, chromium, iron, or other metals which form more than one oxide.[63] Calcium hydroxide or carbonate is added to the water to neutralize the acid and prevent corrosion of the apparatus. The salts thus formed can be recovered. The steam produced in the process may be employed for generating power.

Baum and Herrmann[64] obtained acetylene by means of a hydrogen-oxygen flame in petroleum. A carbon monoxide-hydrogen-oxygen flame in petroleum produced ethane and acetylene. Acetylene may also be produced on burning oxygen or a gas containing oxygen in an atmosphere of hydrocarbon gas or submerged in a liquid hydrocarbon.[65] The yield is affected by the ratio of hydrocarbon to oxygen and also by the shape of the vessel. The yield is greater when the oxygen is supplied through a jet with small diameter than with a large diameter and by supplying the gas through several jets in one vessel than through the same number of jets each in a separate vessel.

SULPHONATED AND CHLORINATED OXIDIZED HYDROCARBONS

Sulphonated[66] and chlorinated[67] oxidized hydrocarbons have found a variety of uses. They have been suggested as emulsifying, wetting, and flotation agents, and as insecticides.

The vapor phase oxidation of a Pennsylvania gas oil distillate gave alcohols, aldehydes, ketones, saturated and unsaturated acids and unchanged hydrocarbons.[68] This mixture, after being sulphonated, washed, and neutralized with sodium hydroxide yielded a composition having 40 per cent oxygen and 1.5 per cent sulphur. It was a clear stable, maroon-colored liquid which easily emulsified with water. A 1 per cent solution was toxic to aphids, leaf hoppers and red mites. As an activator for poisons such as nicotine sulphate it was much more effective than the soaps usually employed.

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[61] U. S. Patent 1,716,433, June 11, 1929; assigned to Ellis-Foster Co.; *Brit. Chem. Abs.* **B**, 1929, 745.

[62] The history and development of submerged combustion is discussed by Hammond, *J. Inst. Fuel*, 1930, **3**, 303. See also *Gas J.*, 1930, **189**, 500; *Gas World*, 1930, **92**, 14; *Chem. Abs.*, 1930, **24**, 2578; *Chem. Age* (*London*), 1927, 274; Hammond (*Fuel Economist*, 1929, **4**, 385; *Chem. Abs.*, 1930, **24**, 1721), Tupholme (*Gas Age Record*, 1929, **64**, 373; *Chem. Abs.*, 1930, **24**, 1721) and Brownlie (*Combustion*, 1930, 1 (12), 46; *Chem. Abs.*, 1931, **25**, 5748) described the uses and advantages of the Hammond submerged combustion burner.

[63] Ormandy, British Patent 296,121, 1927; *Chem. Abs.*, 1929, **23**, 2253. Lutz (German Patent 475,882, 1927; *Chem. Abs.*, 1929, **23**, 3779) produced oxides of nitrogen by burning liquid fuels in the presence of nitrogen and oxygen under pressures of 50-100 atmospheres. Contact agents such as tungsten or titanium were used.

[64] U. S. Patent 1,864,196, June 21, 1932; *Chem. Abs.*, 1932, **26**, 4347; German Patent 568,673, 1927; *Chem. Abs.*, 1933, **27**, 2741; both patents assigned to Consortium für elektrochemische Industrie G.m.b.H.; see also footnote 84 in Chapter 36.

[65] Millar, British Patent 364,418, 1931; *Brit. Chem. Abs.* **B**, 1932, 248; French Patent 713,012, 1930; *Chem. Abs.*, 1932, **26**, 1624; both patents assigned to Bataafsche Petroleum Maatschappij; Millar, U. S. Patent 1,896,552, Feb. 7, 1933; *Chem. Abs.*, 1933, **27**, 2696; Canadian Patent 309,544, 1931; *Chem. Abs.*, 1931, **25**, 2441; both patents assigned to Shell Development Co.

[66] The action of sulphonating agents on hydrocarbons and the production of various other sulphonated derivatives is discussed more completely in Chapter 46.

[67] See also Chapter 30.

Sulphonated products of partially oxidized petroleum hydrocarbons, either as free acids or as alkali salts, can be used as cleansing or emulsifying agents, in the manufacture of lubricants, with flotation oils, or in tanning.[69]

Oxidation products of solid or liquid paraffin or naphthene hydrocarbons, tars, or waxes may be sulphonated with sulphur trioxide[69a] or with oleum or chlorosulphonic acid[69b] to produce emulsifying and wetting agents. These sulphonated products may be improved as textile assistants by addition of electrolytes, such as salts of sodium, potassium, magnesium, ammonium, barium, aluminum or zinc, or water-soluble salts of acids stronger than carbonic.[69c]

Chlorination or sulphonation of the unsaturated hydrocarbons, resulting from the dehydration of oxidized paraffin or waxes, gives substances which form water-soluble salts with bases such as ammonia, pyridine, amines, sodium hydroxide, or sodium carbonate, which are useful as wetting, emulsifying or cleansing agents, and in the preparation of insecticides and disinfectants.[70] The unsaturated liquid hydrocarbons are obtained by first oxidizing liquid or solid paraffin or naphthene hydrocarbons in the presence of barium cinnamate, uranyl tungstate, or manganese naphthenate. The product, which contains a mixture of alcohols, hydroxy-acids, esters, lactones, and other substances, is then heated to 180° C. in the presence of catalysts with the result that water or carbon dioxide is split off and the unsaturated compounds are formed.[71] The use of boric acid or vanadium pentoxide is said to increase the yield of alcohols. Any free acids which still remain in the crude product can be removed in a number of different ways.

A mixture consisting mainly of aliphatic alcohols of 12 to 20 carbon atoms and acids of 11 to 24 carbon atoms, obtained by extracting partially oxidized paraffin hydrocarbons with methyl alcohol, may be reacted with one-third of its weight of 98 per cent sulphuric acid at 35° C. for 2 hours, and the excess sulphuric acid removed by washing with sodium sulphate solution to produce sulphonated products. The resulting material may be mixed with 3 to 4 times its weight of spindle oil and 2 to 3 per cent of ammonia to form a stable emulsion with water, which may be used as a wetting, cleansing and emulsifying agent.[71a] Products for similar purposes may be obtained by sulphonation of oxidized products of mineral oil, ceresin, or tar fractions.[71b]

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[68] Inman, *Ind. Eng. Chem.*, 1929, **21**, 542. See also Hoerner, *J. Econ. Entomol.*, 1930, **23**, 174; *Chem. Abs.*, 1930, **24**, 3314.

[69] James, U. S. Patent 1,753,516, April 8, 1930; *Chem. Abs.*, 1930, **24**, 2591.

[69a] I. G. Farbenindustrie A.-G., French Patent 714,000, 1931; *Chem. Abs.*, 1932, **26**, 1732; see also Chapter 46.

[69b] I. G. Farbenindustrie A.-G., British Patent 303,281, 1928; *Brit. Chem. Abs.* **B**, 1929, 197; see also Chapter 46.

[69c] I. G. Farbenindustrie A.-G., British Patent 352,989, 1930; *Brit. Chem. Abs.* **B**, 1931, 1090; French Patent 703,466, 1930; *Chem. Abs.*, 1931, **25**, 4414; French Patent 40,987, 1931; addition to French Patent 703,466; *Chem. Abs.*, 1933, **27**, 1524; see also Chapter 46.

[70] I. G. Farbenindustrie A.-G., British Patent 321,239, 1928; *Chem. Abs.*, 1930, **24**, 2516; British Patent 324,031, 1928; *Chem. Abs.*, 1930, **24**, 3332; French Patent 673,887, 1929; *Chem. Abs.*, 1930, **24**, 2596.

[71] I. G. Farbenindustrie A.-G., British Patent 357,620; appln. date Jan. 1930; *Chem. Age (London)*, 1931, 134.

[71a] U. S. Patent 1,909,295, May 16, 1933; German Patent 577,428, 1933; *Chem. Abs.*, 1933, **27**, 4043; German Patent 524,354, 1925; *Chem. Abs.*, 1931, **25**, 3664; French Patent 680,351, 1929; *Chem. Abs.*, 1930, **24**, 3798; all patents assigned to I. G. Farbenindustrie A.-G.; see also Chapter 46.

[71b] I. G. Farbenindustrie A.-G., British Patent 373,642, 1932; *Chem. Abs.*, 1933, **27**, 4116; see also Chapter 46.

The sulphonation of hydroxy acids obtained by oxidation of crude montan wax, or amides, anhydrides or esters of montan wax acids, or alcohols or amines corresponding to these alcohols, to produce wetting, cleansing and emulsifying agents has also been suggested.[71c]

Sulphonic acids, which can be used in the hydrolysis of fats, as emulsifying agents, or in the textile industry, are made by sulphonating white oil or liquid paraffin which has been previously oxidized at 140° to 180° C. by a current of air.[72]

Chatrov,[72a] by using different proportions of reagents and temperatures, obtained four different sulphonated derivatives from crude hydroxy acids of oxidized paraffin hydrocarbons. The products were soluble only in sodium hydroxide, and partly in sodium carbonate and carbon disulphide and emulsified with water. The most highly sulphonated acid showed wetting properties, but was not satisfactory as a soap although it could be substituted for sodium ricinoleate in naphthol or lizarol baths for printing with alizarin red or rose.

MISCELLANEOUS PRODUCTS

A medicinal product is obtained when hydrocarbon oils, such as kerosene, are atomized and partially burned with a limited supply of air, and the vapors condensed.[73] The product is described as a liquid of low irritability and high absorbability for medicinal purposes in the treatment of catarrhal diseases.

For preserving wood, Petrov, Danilovich and Rabinovich[73a] suggested forcing oxygen under pressure through the material impregnated with warm hydrocarbon oil, the oxidation taking place in the pores of the wood. An oil-soluble catalyst such as a metallic salt of a fatty acid may be employed.

Compositions which may be used as insecticides or fumigants may be prepared by oxidizing the sulphur dioxide extract of kerosene distillates and emulsifying the resulting products with water.[73b]

A wood preservative[74] which contains aldehydes and aldehyde-acids is prepared by the partial oxidation of petroleum hydrocarbons by passing the oil vapors and air over catalysts at 200° to 500° C. The oxides of molybdenum are used as catalysts, and steam may also be added to the gaseous mixture. The insoluble calcium salts of these acids can be used for waterproofing fabrics or paper making. Soluble soaps are employed for the emulsification of disinfectants or in mixtures for spraying trees.[75] A water emulsion of petroleum oils with the acids from such oils (particularly from the oxidation of naphthenic hydrocarbons) is suggested as a herbicide.[76]

Mineral frothing agents, which may be employed in the concentration of ores, are obtained by the partial oxidation of various petroleum fractions in the liquid phase.[77] Catalysts need not be used during the oxidation step.

[71c] Jahrstorfer and Hummel, German Patent 578,405, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 4435; see also Chapter 46.

[72] Petroff and Shestakoff, U. S. Patent 1,761,744, June 3, 1930; *Brit. Chem. Abs.* **B**, 1931, 332.

[72a] *Rekonstruktsiyu Tekstil. Prom.*, 1932, 11 (4), 48; *Chimie et industrie*, 1932, **29**, 418; *Chem. Abs.*, 1933, **27**, 2305.

[73] Porter, U. S. Patent 1,660,655, Feb. 28, 1928; *Chem. Abs.*, 1928, **22**, 1440.

[73a] German Patent 552,477, 1930; *Chem. Abs.*, 1932, **26**, 4438; Russian Patent 23,595, 1931; *Chem. Abs.*, 1932, **26**, 2034.

[73b] DeOng, Canadian Patent 318,318, 1931; assigned to Shell Development Co.; *Chem. Abs.*, 1932, **26**, 1381; *cf.* Sankowsky and Fulton, British Patent 394,977, 1932; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1933, 760. Yates (*Petroleum Z.*, 1933, **29** (20), 5; *Brit. Chem. Abs.* **B**, 1933, 654) discusses the use of naphthenic acid and phenol fractions of kerosene as disinfectants and insecticides. Martin and Salmon (*J. Agri. Sci.*, 1931, **21**, 638; *Chem. Abs.*, 1932, **26**, 3607) investigated the fungicidal properties of certain sprays prepared from mineral, tar and vegetable oils. Klemgard (*Refiner*, 1929, **8** (6), 58; *Chem. Abs.*, 1929, **23**, 4332) proposed formulas for insecticide sprays as well as for various cleaning fluids and polishes.

[74] James, U. S. Patent 1,561,164, Nov. 10, 1925; *Chem. Abs.*, 1926, **20**, 101.

[75] British Patent 174,099, 1920; *Chem. Abs.*, 1922, **16**, 1878.

[76] DeOng, Canadian Patent 305,502, 1930; assigned to Shell Development Co.; *Chem. Abs.*, 1931, **25**, 768.

Unsaturated acids of high molecular weight, such as are produced by the dehydration of the acids obtained in the oxidation of paraffin wax, when mixed with an alkaline agent, e.g., a solution of ammonia, yields a composition which finds application for the oiling of fibrous materials like wool.[78]

In the manufacture of stove lacquers the residues from the distillation of oxidized paraffin waxes are polymerized by heating with chlorine and sulphur and then dispersed or dissolved in various organic solvents.[79]

Bituminous materials (free of volatile oils) oxidized in the presence of alkalies and emulsified with water furnish a product which can be mixed with cement and used for producing a cold glaze.[80] Before the addition of the oxidized bituminous substance, the cement may be mixed with pigments to obtain glazes of various colors.

The pitch-like residues from the distillation of coal-tar or of petroleum can be air-blown in the presence of manganese dioxide to yield products for impregnating roofing paper.[81] The addition of formaldehyde to the blown residue before cooling is said to aid deodorization and to increase the durability of the product.

Organic acids, suggested as synthetic tanning agents, are obtained by the oxidation of fossil vegetable materials in the presence of nitric acid.[82] Thus, brown-coal residues, e.g., those extracted with benzene, are heated to 90° C. in a covered vessel in a current of air, while fuming nitric acid is allowed to percolate through the mass. When samples of the material show no increase in solubility in water, oxidation is stopped and the nitrous gases removed by a current of air. The product is a mixture of acids, which contain no more nitrogen than the original substance. Ozokerite gives a water-insoluble acid mixture, the sodium salts of which possess soap-like properties.

The oxidation product from paraffin wax, after it has been freed of resins or asphalts, or the acid compounds after being separated from the other oxidation products, or the zinc salts of these products, may be added to synthetic or natural rubber before vulcanization.[83] Or the oxidized products mixed with an accelerator, such as mercaptobenzothiazole, may be employed similarly.[83a]

Oxidized petroleum oils, pine tar, or stearic acid have been added to rubber, before incorporation of reenforcing ingredients and vulcanizing agents, to obtain rubber compositions of increased resistance to abrasion.[83b]

Linseed, or other similar unsaturated oils, can be oxidized by mixing with molten paraffin wax, cooling, powdering the mixture and exposing it to air at ordinary temperatures.[83c] When dispersed in this manner the linseed oil is rapidly oxidized. The wax is subsequently melted and separated from the solid oxidation

[77] Wilkinson, Canadian Patents 246,235, 246,236, 246,237, 246,238, 246,239, 1925; *Chem. Abs.*, 1925, **19**, 1242.

[78] Luther and Beller, U. S. Patent 1,808,363, June 2, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1931, **25**, 4415.

[79] I. G. Farbenindustrie A.-G., British Patent 322,437, 1928; *Brit. Chem. Abs.* **B**, 1930, 827; British Patent 329,954, 1928; *Brit. Chem. Abs.* **B**, 1930, 827.

[80] Friedrich, U. S. Patent 1,402,412, Jan. 3, 1922.

[81] Schreiber, British Patent 7,739, 1907.

[82] Daimler, German Patent 441,432, 1920; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1927, 924.

[83] I. G. Farbenindustrie A.-G., French Patent 703,791, 1930; *Chem. Abs.*, 1931, **25**, 4742; British Patent 352,167, 1930; *Brit. Chem. Abs.* **B**, 1931, 1021.

[83a] Sanderson, Canadian Patent 316,118, 1931; assigned to Goodyear Tire and Rubber Co.; *Chem. Abs.*, 1932, **26**, 1831.

[83b] Cagnon, British Patent 378,197, 1932; assigned to Goodyear Tire and Rubber Co.; *Chem. Abs.*, 1933, **27**, 4130.

[83c] Eisenstein, U. S. Patent 1,564,331, Dec. 8, 1925; assigned to I. G. Schicht A.-G.; *Brit. Chem. Abs.* **B**, 1926, 202.

product. The linseed oil can also be dispersed on sodium chloride, oxidized at 100° C., and the salt removed later by washing with water.

Materials such as sawdust, wood, moss, paper pulp and rags are oxidized by heating in an alkaline solution to which is added a heavy hydrocarbon, for example, paraffin, which appears to act as a catalyst.[83d] Air may be used as the oxidizing agent, at a temperature of about 200° C. Salts of oxalic and other organic acids are the principal products of this oxidation.

BACTERIAL OXIDATION OF CRUDE OILS

In a study of the bacterial oxidation of crude oils, Tauson[84] found that *Penicillium* develops on paraffins melting at 45° to 56° C., and utilizes about 80 per cent of the hydrocarbon, *B.fluorescens liquifaciens, B.pyocyaneus, B.stutzeri* and other bacteria utilize paraffins as well as kerosene, and microorganisms obtained from the Baku region (bacteria as well as the mold *Aspergillus flavus*) can utilize both hard and soft paraffin as well as white vaseline. The paraffins are oxidized to carbon dioxide and water, there being no evidence of the production of fatty acids. Hydrocarbons of the olefin group are apparently easily oxidized, and the oxidation of terpenes also seems very probable. Conditions necessary for oxidation of the paraffins are: (1) The presence of an aqueous solution of mineral salts, including a nitrate or ammonium salts. In the case of the latter, calcium carbonate must be present to neutralize the acid set free by the liberation of ammonia. (2) The reaction of the solution must be as nearly neutral as possible, and (3) there must be a free access of oxygen. Other bacteria oxidize aromatic substances. For example, benzene, toluene, and xylene are oxidized by *B.benzoli*, naphthalene by *B.naphthalinicus liquifaciens, B.naphthalinicus*, and *B.naphthalinicus nonliquifaciens*, and phenanthrene by *B.phenanthrenicus*. Since the soil in oil-bearing regions is rich in a great variety of microörganisms which utilize hydrocarbons and display considerable specificity, and also because the conditions for this growth are very frequently found, it was concluded by Tauson that bacterial action plays a very important rôle in those changes of the crude oil which take place before it comes from underground.

[83d] Mellanoff, British Patent 307,784, 1928; assigned to Kemikal, Inc.; *Chem. Abs.*, 1930, **24**, 128.

[84] *Neft. Khoz.*, 1928, **14**, 220; *Brit. Chem. Abs.* **A**, 1929, 1108; *Chem. Abs.*, 1929, **23**, 1431.

Chapter 46

Action of Sulphonating Agents on Petroleum Hydrocarbons. Sulphonic Acids, Detergents, and Other Products

The action of sulphonating agents such as concentrated or fuming sulphuric acid on petroleum hydrocarbons is of considerable interest in view of the large-scale application of sulphuric acid in the refining of petroleum distillates. The various classes of hydrocarbons behave in markedly different ways toward this reagent. In general, when combination occurs, two main reactions may be distinguished, namely, *sulphation* and *sulphonation*. The former, which is exemplified by the interaction of unsaturated hydrocarbons with sulphuric acid, yields a sulphuric acid ester in which a carbon atom is linked through an oxygen atom to a sulphur atom, i.e., in compounds of the type $R—O—SO_3H$. These sulphuric acid esters are distinguished by their ready hydrolysis to alcohols (see Chapters 13, 14 and 16). On the other hand, the true sulphonated products contain a carbon atom directly linked to a sulphur atom which is itself part of a sulphonic, or $—SO_3H$, group. This carbon-sulphur linkage is much more stable than the carbon-oxygen linkage and even alkylsulphonic acids of the type $R^1R^2R^3—C—SO_3H$ are extremely resistant to hydrolytic influences.[1]

The action of sulphuric acid on hydrocarbons not only forms sulphates or sulphonates, however, but also induces polymerization and oxidation reactions (which have been discussed in Chapters 26 and 37). The unsaturated hydrocarbons are polymerized in the presence of this acid, particularly with high concentrations of acid. With very concentrated or fuming sulphuric acid, oxidation of the hydrocarbon molecule often results, in which the sulphuric acid or sulphur trioxide is itself reduced to sulphur dioxide. Many of the stable paraffin and cycloparaffin hydrocarbons are oxidized as well as sulphonated on treatment with warm fuming sulphuric acid or sulphur trioxide.

As already indicated in Chapter 13, the unsaturated hydrocarbons of the olefin series generally undergo sulphation, with the production of esters, when subjected to the action of sulphuric acid. However, polymerization is often the main result of treatment of olefins with this acid, particularly if the acid is very concentrated. Even more pronounced is the action of sulphur trioxide on olefin hydrocarbons, which induces both polymerization and oxidation. The reaction of olefins with sulphuric acid to form derivatives of carbyl sulphate [2] is discussed in this chapter.

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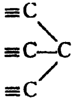
[1] These differences are pointed out also by Hart, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 411. *Cf.* Stadlinger, *Chem. Umschau*, 1932, **39**, 217; *Chem. Abs.*, 1933, **27**, 3840; Lindner, Russe and Beyer, *Fettchem. Umschau*, 1933, **40**, 93; *Chem. Abs.*, 1933, **27**, 3838. Kalinor and Schmidt (*Chimie et industrie*, 1933, **29**, 1278; *Brit. Chem. Abs.* **B**, 1933, 718) made a further distinction: those sulphonic acids having a sulphonic acid group in the middle of the chain are called "internal" whereas those having one at the end are called "external." The numerous proposals for the treatment of different stocks with sulphuric acid of various strengths appear in many cases to use the term "sulphonated" rather loosely. Generally, however, the word has the significance of its usual meaning, namely, that involving direct linkage of sulphur to carbon. Luther, however, stated that under the term "sulphonated" as used by him in U. S. Patent 1,908,376 he included the products which have been acted upon by sulphonating agent so that either sulphuric esters or sulphonic acids or mixtures of both may be obtained, depending on the character of the sulphonating treatment. Perhaps, from the standpoint of this chapter, the term "sulpho compounds" as used by a number of investigators could be applied conveniently in a generic sense. Gray, for instance, stated ("The Mineral Industry," 1901, 579): "In the treatment of oils with sulphuric acid, considerable action takes place and the reaction is a very complex one. The acid removes the asphaltic matter and attacks and combines with many hydrocarbons forming 'sulpho' compounds." At the risk of some confusion, the author has been impelled to adopt the terms reported to have been used by the investigator or investigators in each case.

The most readily sulphonated hydrocarbons are those of the aromatic series. The aromatic sulphonic acids are in most cases prepared by warming the aromatic hydrocarbon with concentrated sulphuric acid. The conversion of benzene into its monosulphonic acid is a typical reaction, and proceeds as follows:

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$$

The aromatic sulphonic acids derived from benzene and naphthalene and their immediate homologues and derivatives find extensive application in the manufacture of dyestuffs. An extended discussion of the sulphonation of aromatic hydrocarbons, however, is outside the scope of this book. The relatively greater ease of sulphonation of the typically aromatic hydrocarbons as a class should, nevertheless, be noted and a few instances will be cited in which aromatic hydrocarbons present in petroleum appear to have been sulphonated.

Comparatively little work has been carried out on the sulphonation of saturated hydrocarbons of the paraffin and cycloparaffin series, but the indications are that most of these hydrocarbons, despite their apparently great resistance to chemical action, can be sulphonated by fuming sulphuric acid, oxidation also occurring in the presence of this reagent. Certain types of saturated hydrocarbons, notably those containing a tertiary carbon atom, i.e., the grouping  $\begin{matrix}\equiv C & \\ \equiv C & -CH \\ \equiv C & \end{matrix}$, appear to be much more readily sulphonated (and also nitrated) than their straight-chain isomers.

Since immense quantities of petroleum hydrocarbons are refined with sulphuric acid, during which process considerable formation of sulphonic acids takes place, this action of sulphuric acid on hydrocarbons is of importance. These sulphonic acids derived from mineral oils have attracted a high measure of technical interest. The acid refining of gasoline distillates is usually accomplished under conditions which preclude attack of all but the most reactive constituents, and are such that probably no saturated aliphatic hydrocarbons are sulphonated. However, the conditions are somewhat more severe in the acid refining of certain lubricating distillates, and even treatment with fuming sulphuric acid is resorted to in the manufacture of petrolatum. Undoubtedly, under the latter conditions, considerable sulphonation and oxidation of the more reactive saturated (paraffin and cycloparaffin) hydrocarbons can, and does, take place. Our knowledge of the sulphonation of the saturated hydrocarbons is largely limited to that of hydrocarbons of comparatively low molecular weight. Only inferences can be drawn from these data concerning the reactions which occur in the acid refining of higher petroleum fractions. It appears that the saturated hydrocarbons present in the higher distillates of many petroleums are much more reactive toward chemical reagents, sulphuric acid included, than the simpler saturated compounds and that the almost

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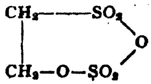
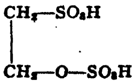
[2] Carbyl sulphate,  $\begin{matrix} CH_2-SO_2 \\ | \\ CH_2-O-SO_2 \end{matrix}$ O, is the anhydride of ethionic acid,  $\begin{matrix} CH_2-SO_3H \\ | \\ CH_2-O-SO_3H \end{matrix}$

unknown class of polynuclear cycloparaffins may embrace more highly reactive hydrocarbons than has hitherto been suspected.

Although the sulphonation of saturated hydrocarbons is primarily of interest in connection with the acid refining of petroleum distillates, another aspect of the question should not be overlooked. Since the saturated aliphatic and saturated cyclic sulphonic acids can be made the starting point of a number of syntheses (for example, the conversion into alcohols by hydrolysis or lower carboxylic acids by alkali fusion), it may be possible to utilize the sulphonation process as a method of transforming the more readily sulphonated paraffins and cycloparaffins into derivatives with desirable properties. It is unfortunate that our knowledge of the sulphonation of even the simpler paraffins and cycloparaffin hydrocarbons is so exceedingly meager.

Sulphonation of Paraffin Hydrocarbons

Most of the simpler paraffin hydrocarbons appear to be unattacked in the cold by concentrated sulphuric acid (up to 100 per cent H_2SO_4). However, McKee[3] stated that saturated hydrocarbons of ordinary Pennsylvania kerosene fraction which boiled at about 200° C. could be sulphonated to disulphonic acids by ordinary concentrated sulphuric acid with vigorous stirring (900 revolutions per minute). Brooks and Humphrey[4] were unable to verify this; both pure n-heptane and diisopropyl were unaffected by shaking with 95 per cent sulphuric acid (specific gravity 1.84) at 25° C. for 48 hours.

Paraffin hydrocarbons are absorbed in cold fuming sulphuric acid. For example, Orndorff and Young[5] found that propane was absorbed to the extent of 50 per cent in 50 days. Worstall[6] observed that ethane was absorbed more rapidly than methane by fuming sulphuric acid. The absorption of methane, ethane, propane, butane, isobutane, pentane, hexane, isopropylethane, heptane, ethylisoamyl, and octane in fuming sulphuric acid of various concentrations has also been determined.[7] Mabery[8] noted that various fractions of Pennsylvania petroleum were dissolved by fuming sulphuric acid. Other results on the absorption of constituents of gasolines and petroleum distillates in sulphuric acid of several concentrations were given by Ormandy and Craven[9] and Carpenter.[10]

Fuming sulphuric acid reacts with some paraffin hydrocarbons to yield sulphonic acids. An investigation of the action of fuming sulphuric acid on n-hexane, n-heptane and n-octane was carried out by Worstall.[11] He found that although these hydrocarbons were unaffected by cold fuming acid, rapid sulphonation occurred when the acid was added to the boiling hydrocarbons. The products consisted of monosulphonic acids together with smaller proportions of disulphonic acids. Better yields of the latter were obtained by passing sulphur trioxide into the boiling hydrocarbons. The hexane-monosulphonic acid, the yield of which was about 30 to 40 per cent of the theoretical, was a light brown liquid, very soluble in alcohol and water but insoluble in ether. Considerable oxidation of the hydrocarbons took place in the sulphonation. The disulphonic acids produced by the action of sulphur trioxide on the boiling hydrocarbons were dark syrupy liquids. In addition to the disulphonic acids, brown brittle solids, insoluble in water and all organic solvents, were isolated. These solid products Worstall considered were probably oxysulphones.

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[3] Paper delivered at A. C. S. meeting in Washington, D. C., 1911; *Chem. Ztg.*, 1912, 36, 872.

[4] *J.A.C.S.*, 1918, 40, 847.

[5] *Amer. Chem. J.*, 1893. 15, 249; *Chem. Soc. Abs.*, 1893. 64 (1), 498.

[6] *J.A.C.S.*, 1899, 21, 245.

[7] Grimm, Dissertation, Karlsruhe-Basel, 1897; Lehmann, Dissertation, Karlsruhe-Freiburg, 1897; Sentke, Dissertation, Karlsruhe, 1907; see Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 231. *Cf.* Tropsch and Dittrich, *Brennstoff-Chem.*, 1925, 6, 169; *Ges. Abhandl. Kenntnis Kohle*, 1929, 8, 285.

[8] *Proceedings, Amer. Acad.*, 1902, 37, 565; *Amer. Chem. J.*, 1902, 28 (3), 165; *J.S.C.I.*, 1902, 21, 1271.

[9] *J. Inst. Pet. Tech.*, 1926, 12, 68; *Chem. Abs.*, 1926, 20, 2581.

[10] *J. Inst. Pet. Tech.*, 1926, 12, 518; *Chem. Abs.*, 1927, 21, 1702; see also Chapter 49 for additional references.

[11] *Amer. Chem. J.*, 1898, 20, 664; *Chem. Soc. Abs.*, 1899, 76 (1), 18.

Burkhardt and Lapworth[12] observed that sulphur trioxide attacked ligroin and crude hexane completely in the cold, considerable sulphur dioxide being evolved. This led to an investigation by Burkhardt[13] of the action of fuming sulphuric acid on n-hexane and cyclohexane. By vigorously stirring n-hexane with fuming sulphuric acid (35 to 65 per cent free SO_3) at 0° to 10° C., almost all the sulphur trioxide was consumed in the resulting reaction, and approximately 1 molecule of sulphur dioxide was formed for each molecule of hydrocarbon attacked. Isolation of individual substances from the complex mixture of barium salts, obtained by neutralization of the acid layer with barium carbonate, was not effected. The general nature of the products was determined from the analytical data of the mixed barium salts (and the derived sulphonyl chlorides). Partial separation of the mixed salts was made by fractional precipitation from their concentrated aqueous solutions with alcohol. The mixed barium salts from n-hexane were partly unsaturated and contained sulphuric acid ester groups, probably as salts of sulphato-sulphonic acids formed by the action of fuming acid on the unsaturated compounds produced by initial oxidation. After hydrolysis of these substances, the products contained 2 molecules of disulphonic acids to 1 molecule of monosulphonic acid. About 5 per cent of the hexane chains were unsaturated and 30 per cent contained a hydroxyl group. It is evident, therefore, that fuming sulphuric acid both oxidizes and sulphonates hexane. Burkhardt believed that the oxidation probably leads to the formation of an unsaturated hydrocarbon which is immediately sulphonated by the acid to a sulphuric ester. Hydrolysis of these sulphato-sulphonic acids then yields sulphonated compounds containing either an unsaturated linkage or a hydroxyl group.

According to Brooks and Humphrey,[14] hydrocarbons containing a tertiary hydrogen group, such as diisopropyl, are much more readily sulphonated and oxidized than straight-chain members. They regard it very possible that the large losses experienced in the refining of mineral lubricating oils by concentrated sulphuric acid may be partly attributed to sulphonation and oxidation of such branched-chain hydrocarbons. It is interesting to note at this point that in 1875 Vohl[15] found as much as 3.1 per cent of sulphuric acid (probably as esters) in American cracked kerosene.

The sulphonation of various higher-boiling distillates with fuming sulphuric acid is discussed in the section on the production of mineral oil sulphonic acids. Very little is known of the reaction or constitution of the products formed. Gill and Meusel,[16] as early as 1868, observed that fuming sulphuric acid had no effect on a paraffin which melted at 60° C. and contained 85.5 per cent carbon and 14.9 per cent hydrogen. However, Istrati and Michailescu[17] noticed that paraffin waxes of high melting points, when cautiously heated with sulphuric acid, reacted without the formation of coke. No sulphonic acids were obtained but they did observe the evolution of carbon dioxide and sulphur dioxide which resulted from partial

[12] *J.C.S.*, 1926, 684.
[13] *J.C.S.*, 1930, 2387.
[14] *J.A.C.S.*, 1918, 40, 822; *cf.* Brame, Dunstan, Lomax, Pemberton, Craven and Moore, *J. Inst. Pet. Tech.*, 1926, 12, 48.
[15] *Dingler's Polytech. J.*, 1875, 216, 47.
[16] *J.C.S.*, 1868, 21, 466; *Chem. Zentr.*, 1869, 305.
[17] *Bull. soc. sci. Bucharest*, 1904, 13, 143; *Chem. Zentr.*, 1904, 2, 1447.

decomposition by oxidation. From this behavior they concluded that the various paraffins contain a large number of branched-chain isomers.[18]

The action of *chlorosulphonic acid* [$SO_2(OH)Cl$] on the paraffins often produces sulphonated products, hydrogen chloride being eliminated during the process.[19] Aschan [20] found that diisopropyl reacted with chlorosulphonic acid at room temperature with the evolution of hydrogen chloride, and abundant heat production. The reaction was regarded by Aschan to be of a complicated character for, besides sulphonated products, a considerable amount of unsaturated oily material was formed. Isopentane also reacted with chlorosulphonic acid in a similar way. The relative ease with which many branched-chain hydrocarbons are sulphonated by this reagent has been used by Young,[21] and later by Shepard, Henne and Midgley [22] to obtain straight-chain paraffins free from the more reactive branched-chain members and naphthenes.

SULPHONATION OF CYCLOPARAFFINS

The naphthenes react with fuming sulphuric acid, resulting both in sulphonation and oxidation.[23] Concentrated sulphuric acid, however, has no effect in the cold, except on the lower members of the series.[24] With an excess of sulphuric acid, at ordinary temperatures or more readily at 40° C., some cycloparaffins yield aromatic mono- and di-sulphonic acids, resins, and products volatile with steam.[25]

Of the cycloparaffins, the cyclopropane derivatives appear to be most readily attacked. Treatment of cyclopropane or its homologues with even moderately concentrated sulphuric acid usually results in rupture of the ring and the formation either of sulphuric esters of a straight-chain alcohol or of polymerized straight-chain olefins. Thus, cyclopropane itself is absorbed by concentrated sulphuric acid to the extent of 480 cc. of cyclopropane per gram of acid at 18° C.[26] Dilution of the acid solution followed by distillation affords propyl alcohol.[27] Absorption of methylcylcopropane in concentrated sulphuric acid results in the formation of a mixture of high-boiling polymers (evidently derived from the corresponding butene) and, if the solution is diluted, secondary butanol is formed on distillation.[28] 1,1-Dimethylcyclopropane also dissolves in dilute sulphuric acid (2 volumes of acid and 1 volume of water).[29]

Cyclohexane itself gives no indication of being attacked by concentrated sulphuric acid but treatment with fuming sulphuric acid results in oxidation and sulphonation. Burkhardt[80] treated cyclohexane and methylcyclohexane with fuming sulphuric acid (35 to 65 per cent free SO_3) at 0° to 10° C. and observed the formation of sulphur dioxide to the extent of about 1 molecule per molecule of hydrocarbon attacked. As in the case of n-hexane, the products consisted of sulphato-sulphonic acids (probably derived from unsaturated hydrocarbons), which on hydrolysis yielded both mono- and di-sulphonic acids, often containing an ethylene linkage or a hydroxyl group. Small amounts of benzenesulphonic acids were also noted by Burkhardt in the sulphonation of cyclohexane.

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[18] See their previous work (*Bull. soc. sci. Bucharest*, 1897, **6**, 61; *Chem. Zentr.*, 1897, 1, 1222) on an ozokerite (m.p. 97-98° C.) which also gave no sulphonic acids on heating with concentrated sulphuric acid.

[19] The sulphonation of the more reactive paraffins by chlorosulphonic acid apparently proceeds according to the typical equation $C_6H_{14} + ClSO_3H \rightarrow C_6H_{13}SO_3H + HCl$. On the other hand, chlorosulphonic acid reacts with *aromatic hydrocarbons* and their derivatives with the formation of *sulphonyl chlorides*. Thus benzene and chlorosulphonic acid at 150°-160° C. yield benzene-1,3-disulphonyl chloride according to the equation $C_6H_6 + 2ClSO_3H \rightarrow C_6H_4(SO_2Cl)_2 + 2H_2O$ (Pollak, Heimberg-Krauss, Katscher and Lustig, *Monatsh.*, 1930, **55**, 358; *Chem. Abs.*, 1930, **24**, 4004).

[20] *Ber.*, 1898, **31**, 1801.

[21] *J.C.S.*, 1899, **75**, 172.

[22] *J.A.C.S.*, 1931, **53**, 1948; *Ind. Eng. Chem.*, 1930, **22**, 356.

[23] For reviews of the sulphonation of the naphthenes see Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1892, **24**, 141; *J. prakt. Chem.*, 1892, (2) **45**, 561; *ibid.*, 1892, (2) **46**, 86; *Chem. Soc. Abs.*, 1892, **62**, 1182, 1311; Tilitschejev and Dumiskaja, *Neft. Khoz.*, 927, **13**, 647; *Brit. Chem. Abs.* B, 1928, 630.

[24] Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1898, **30**, 151; *Chem. Zentr.*, 1898, 2, 578; *Ann.*, 1898, **302**, 1; *Chem. Soc. Abs.*, 1899, **76** (1), 22; Aschan, *Ber.*, 1899, **32**, 1769; Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1904, **35**, 1023; *Chem. Zentr.*, 1904, 1, 1345; *Ann.*, 1904, **336**, 299; *ibid.*, 1905, **341**, 118; *Chem. Soc. Abs.*, 1905, **88** (1), 760.

[25] Markownikow, *loc. cit.*; Markownikow and Spady, *Ber.*, 1887, **20**, 1850; Ishevski, *Chem. Ztg.*, 1888, **12**, 1322; Konovalov, *Chem. Ztg.*, 1890, **14**, 113, 145; *Chem. Zentr.*, 1890, 1, 426, 585; Markownikow and Rudevitsch, *J. Russ. Phys.-Chem. Soc.*, 1898, **30**, 586; *Chem. Zentr.*, 1899, 1, 176; Rudevitsch, *J. Russ. Phys.-Chem. Soc.*, 1893, **25**, 385; *Chem. Zentr.*, 1893, **2**, 857.

[26] Berthelot, *Annales de chimie et physique*, 1895, (7) **4**, 102.

[27] Gustavson, *J. pr. Chem.*, 1887, (2) **36**, 300; *Chem. Soc. Abs.*, 1888, **54**, 240.

[28] Demjanow, *Ber.*, 1895, **28**, 21.

[29] Gustavson and Popper, *J. pr. Chem.*, 1898, (2) **58**, 458; *Chem. Soc. Abs.*, 1899, **76** (1), 263.

A similar result was obtained by Menschutkin and Wolf.[81] They observed that 1 gram of cyclohexane reacted with 27 grams of 25 per cent fuming sulphuric acid at 25° C. From the dark brown aqueous extract of the reaction product they isolated 70 per cent of barium salts of aromatic sulphonic acids. The action with anhydrous sulphuric acid was entirely comparable to that of fuming acid. This reaction indicates dehydrogenation of the naphthene to an aromatic compound.

Methylcyclohexane is not attacked at room temperature by concentrated sulphuric acid but fuming acid oxidizes it, and yields little or no sulphonic acids, according to Markownikow.[82] Burkhardt observed that methylcyclohexane was attacked by fuming sulphuric acid (35 to 65 per cent free SO) somewhat more rapidly and more extensively than cyclohexane, with the liberation of about ½ molecule of sulphur dioxide from each molecule of hydrocarbon. The products obtained were similar to those from cyclohexane.

Octanaphthenes react with fuming sulphuric acid, particularly on heating, to give both sulphonation and oxidation products. Markownikow and Spady,[83] for example, obtained 4 grams of barium sulphonate (from which m-xylene could be separated by distillation with steam) by the action of fuming sulphuric acid on 5 grams of 1,3-dimethylcyclohexane after its complete solution at 50° to 60° C. The conversion of 1,2,4-trimethylcyclohexane into pseudocumenesulphonic acid under similar conditions was described by Konowalow.[84]

1,4-Dimethyl-2-ethylcyclopentane dissolved in fuming sulphuric acid (containing 10 per cent sulphur trioxide), with darkening, according to Zelinsky.[85] Little heat is liberated and no sulphur dioxide was evolved, a behavior unlike that exhibited by derivatives of cyclohexane.

The action of chlorosulphonic acid on the cycloparaffins has also been studied. Aschan[86] found that by treating cyclohexane at 60° C. with chlorosulphonic acid, both hydrogen chloride and sulphur dioxide were evolved. The products consisted of unsaturated compounds which resinified on standing but no sulphonic acids were isolated. Methylcyclohexane reacted similarly but at room temperature.

In summarizing the action of sulphonating agents on cycloparaffins it can be said that, in general: (1) The lower cycloparaffin homologues, on treatment with concentrated sulphuric acid, dissolve readily, at the same time these cycloparaffins undergo rearrangement, for the solutions on hydrolysis yield aliphatic alcohols. (2) The higher cycloparaffins are not attacked by concentrated sulphuric acid at ordinary temperatures but are dehydrogenated by fuming acid. The cyclohexane derivatives thus yield aromatic sulphonic acids.

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[80] *J.C.S.*, 1930, 2387.

[81] *Neft. Khoz.*, 1927, 13, 340; *Chem. Abs.*, 1928, 22, 2744; *J. Czechoslov. Chem. Comm.*, 1930, 2, 396; *Chem. Abs.*, 1930, 24, 4510.

[82] *J. Russ. Phys.-Chem. Soc.*, 1903, 35, 1035; *Chem. Zentr.*, 1904, 1, 1345; *Ann.*, 1905, 341, 131; *Chem. Soc. Abs.*, 1905, 88 (1), 760.

[83] *Ber.*, 1887, 20, 1850.

[84] *J. Russ. Phys.-Chem. Soc.*, 1890, 22, 9; *Ber.*, 1890, 23, 431Ref.

[85] *Ber.*, 1923, 56B, 1718, 1723.

[86] Paper given at meeting of Finnish Chemical Society at Helsingfors, Apr. 14, 1905; *Chem. Ztg.*, 1905, 29, 747; see also Aschan, "Chemie der alicylischen Verbindungen," F. Vierweg und Sohn, Braunschweig, 1905, 394.

PROPERTIES OF MONOSULPHONIC ACIDS DERIVED FROM PARAFFINS

The aliphatic sulphonic acids are strongly acidic, stable compounds which are usually obtained in the form of viscous, very hygroscopic liquids. They exhibit the usual properties of sulphonic acids and are readily converted into sulphonyl chlorides and sulphonamides. The carbon-sulphur linkage in these compounds is not broken by the usual hydrolyzing agents but by heating with aqueous alkali at 310° to 375° C., hydrolysis takes place with the formation of an alcohol and sodium sulphite, according to the equation $RCH_2SO_3Na + NaOH \rightarrow RCH_2OH + Na_2SO_3$. This main reaction is also accompanied by decomposition of the resulting alcohol according to the equation $RCH_2OH + NaOH \rightarrow RCOONa + 2H_2$. Wagner and Reid[37] examined this reaction for the sodium salts of a number of normal and secondary saturated aliphatic sulphonic acids. They obtained the results in Table 156 for the percentage decomposition of these salts when heated (in the form of approximately molar solutions) with a 3.7N NaOH solution at 345° C. for 3 hours.

TABLE 156.—*Decomposition of Sodium Salts of Saturated Aliphatic Sulphonic Acids.*

Sulphonic Acid	Decomposed Per Cent	Sulphonic Acid	Decomposed Per Cent
Methyl	1.5	Amyl	13.3
Ethyl	62.7	sec-Amyl	64.2
Propyl	20.2	Hexyl	11.7
Isopropyl	88.6	sec-Hexyl	54.9
Butyl	17.3	Benzene	5.0
sec-Butyl	75.2		

It will be seen that although methylsulphonic acid is by far the most stable, the stability of both the normal and secondary series of acids increases with increasing number of carbon atoms from C_2 to C_6. The secondary acids are less resistant to this hydrolysis than the corresponding normal acids.

A series of sulphonic acids was prepared by Noller and Gordon[38] by oxidation of lead mercaptides with nitric acid. The melting points of the anhydrous sulphonic acids, their monohydrates, and their benzylaniline salts[39] were as follows:

TABLE 156a.—*Melting Points of Sulphonic Acids and Derivatives.*

Sulphonic Acid	Anhydrous Acid ° C.	Monohydrate ° C.	Benzylaniline Salt ° C.
Nonyl	—	—	90.5–91.0
Decyl	—	—	84.0–84.5
Undecyl	49	40–41	84.6–84.7
Lauryl	52	43–45	—
Tridecyl	58	48–49	87.5–88.0
Myristyl	65.5	55–56	82.5–82.7

SULPHONIC ACIDS PRODUCED FROM HIGHER PETROLEUM DISTILLATES DURING REFINING

Concentrated sulphuric acid is the most important reagent for the refining of various petroleum distillates. Although there is an increasing tendency to displace this method in favor of refining processes which depend upon the use of adsorbent materials, Kalichevsky and Stagner,[40] expressed the opinion that, because of its cheapness and its almost universal applicability, it will continue to maintain this leading position for many years in the future. The precise action of the sulphuric acid in the refining process depends largely upon the character of the distillate, the time of treatment, and the amount and concentration of the acid. The refining action of the sulphuric acid involves both chemical reaction and physical solution. When highly unsaturated compounds are present, sulphation and polymerization reactions undoubtedly occur, but under certain circumstances sulphonation of the aromatic constituents also takes place.[41] However, the removal of sulphur compounds, asphaltic materials and naphthenic acids by sulphuric acid appears in most cases to involve purely physical phenomena rather than chemical combination.[42]

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[37] *J.A.C.S.*, 1931, 53, 3407; *Brit. Chem. Abs.* A, 1931, 1268.

[38] *J.A.C.S.*, 1933, 50, 1090.

[39] The salts of benzylmorphine with alkylsulphonic acids of low molecular weight are also easily crystallizable and soluble (Chem. Fabrik vorm. Sandoz, French Patent 709,787, 1930; *Chem. Abs.*, 1932, 26, 1066; *cf.* also Stoll and Burckhardt, U. S. Patent 1,892,019, Dec. 27, 1932; *Chem. Abs.*, 1933, 27, 1894).

The formation of sulphonated products is, as might be expected, at a maximum in the drastic refining of heavier fractions of petroleum for the production of white oils and medicinal paraffins. Even under the less stringent conditions employed in the production of ordinary high-grade lubricants, a certain amount of sulphonation occurs nevertheless. According to Weir, Houghton, and Majewski,[43] there is reason to believe that the following are the changes which take place during the acid refining of solar reduced oil with concentrated acid: (1) the formation of indicator-like substances; (2) the flocculation and adsorption of (colloidally?) dissolved bitumens; (3) solution of other color substances containing chromophoric groups; and (4) some sulphonation and oxidation.

Dunstan and Thole[44] and others showed that most lubricating oils contain 20 to 40 per cent of reactive hydrocarbons which are partially removed from the oil by agitation with sulphuric acid. The resulting acid tars, or sludges, tend to become solid. The fact that these reactive hydrocarbons (which can be concentrated by solution in liquid sulphur dioxide) cannot be hydrogenated by known means to yield fully saturated substances and that their iodine values are exceedingly ill-defined, leads to the presumption that they are not unsaturated hydrocarbons of the types known to us at present but are probably polynuclear naphthenes with unstable groupings or "bridged" structures. As previously noted, Brooks and Humphrey[45] considered it very possible that the extensive oxidation and sulphonation which occur in the acid refining of some heavier petroleum distillates is a result of the attack of certain of the more reactive saturated hydrocarbons, such as paraffins and cycloparaffins with reactive groupings (i.e., a tertiary carbon atom). Because the more reactive constituents of lubricating oil fractions, which are removed or destroyed by drastic acid refining, often possess desirable lubricant properties, the modern tendency is to avoid unnecessarily drastic treatment so as to minimize the elimination of these desirable constituents. Sulphuric acid refining tends to remove the valuable olefins from gasoline also.[46]

The production of sulphonated and oxidized products becomes very pronounced during the manufacture of very highly refined oils of the type of medicinal paraffin (petrolatum liquidum). For the production of such oils, oleum or fuming sulphuric acid is usually employed, the amount of such acid used depending upon the degree of refining desired. According to Holmes,[47] for example, white petrolatum is produced by treating a suitable petroleum distillate with fuming sulphuric acid at an elevated temperature, usually up to 170° C. In the manufacture of technical or medicinal white oils, treatment of lubricating oil stocks with 5 to 10 per cent of oleum has been recommended.[48] Under such stringent conditions, considerable sulphonation and oxidation of the more reactive types of saturated hydrocarbons is to be anticipated.

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[40] "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933, 31.

[41] The action of sulphonating agents on olefins is discussed in a later section of this chapter.

[42] For a complete account of the chemistry of refining, the book of Kalichevsky and Stagner (*loc. cit.*) should be consulted.

[43] *Ind. Eng. Chem.*, 1930, **22**, 1293.

[44] *J. Inst. Pet. Tech.*, 1917, **4**, 191; also Chapter 49 and Kalichevsky and Stagner, *op. cit.*

[45] *J.A.C S.*, 1918, **40**, 822.

[46] Kalichevsky and Stagner, *loc. cit.*; Kaudela, *Brennstoff-Chem.*, 1929, **10**, 404; *Brit. Chem. Abs.* **B**, 1929, 1004; Egloff, *Chem. Met. Eng.*, 1917, **17**, 156.

PRODUCTION AND RECOVERY OF MINERAL OIL SULPHONIC ACIDS AND OTHER PRODUCTS

Sulphuric acid refining of petroleum distillates gives sludges which usually contain, in addition to free acids, polymerized bodies, asphaltic materials, and oxidized substances, together with various sulphonated products. In the disposal of this acid sludge, which has long been a problem to the refiner, the acid is usually separated by the addition of water and reconcentrated for further treatment of distillates. The residual material is largely used as a fuel.[49]

The chemical and physical nature of the sludge, as is quite evident, is dependent upon the character of the original distillate and the refining treatment. Methods for the recovery of sulphonic acids vary with the character of the sludge and with the type of product desired. The sulphonic acids can be separated from acid sludge usually by some selective action such as that of solvents or adsorbents or they can be salted out in the form of their alkali or alkaline earth salts. It becomes extremely difficult and hazardous to generalize concerning these procedures. The most that can be said about some of them is that with a particular sludge, the products removed in the described way can be used for certain definite purposes. Obviously, much of the detail of the individual operations must be omitted here.

As early as 1863, Millochan[50] recovered an oil which could be used in paints as a substitute for linseed and other oils. He mixed 40 per cent of water with acid sludge and allowed it to settle into two layers. The oily layer was then washed with a solution of sodium or potassium hydroxide.

A dyestuff was made by Frasch[51] from crude oil or acid sludge by the action of sulphuric acid. This product was soluble in water, alcohols and acetone and dyed silk or wool a yellow color. Its calcium and alkali salts were soluble in water and could be used for a similar purpose. Forward and Davidson[52] proposed to treat crude petroleum, petroleum tar, or heavy hydrocarbon oil with sulphuric acid in such a way that when heated to 425° C. (800° F.) for 4 to 8 hours, asphalt was produced.

Sulphoparaffins were obtained by Kaufmann[53] by heating acid sludge with a solution of sulphur in petroleum ether at 200° to 250° C. with stirring.

The production of Russian mineral oil, a clear white pharmaceutical oil, required considerable refining with sulphuric acid or anhydride of high concentrations. In these treatments large quantities of sulphonic acids were produced.[54] Great interest was manifested in the recovery and utilization of such sulphonated petroleum derivatives at an early date in Russia, where the industry was concentrated. To extract sulphonic acids from petroleum oils, which have been treated with sulphuric acid or anhydride, Petroff[55] used such solvents as aqueous solutions of methyl and ethyl alcohol or acetone. The sulphonic acids could be recovered from the acid sludge by extraction of the hydrocarbons with gasoline, carbon disulphide, or similar water-immiscible solvents.[56] The sulphonated products were called "kontakt."[57]

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[47] U. S. Patent 1,733,597, Oct. 29, 1929; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, **24**, 495; *cf.* Gallagher, U. S. Patent 1,791,926, Feb. 10, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 1002.

[48] Reddish and Myers, British Patent 347,164, 1929; *Brit. Chem. Abs.* **B**, 1931, 751.

[49] See Kalichevsky and Stagner, *op. cit.*

[50] U. S. Patent 37,918, March 17, 1863.

[51] U. S. Patents 518,989 and 518,990, May 1, 1894; assigned to Grasselli Chemical Co.; British Patents 10,321, 10,322 and 10,323, 1893; *J.S.C.I.*, 1893, **12**, 756; German Patents 84,626 and 87,974, 1893; *Chem. Zentr.*, 1896, **1**, 1040; *ibid.*, 1896, **2**, 1144; *Z. angew. Chem.*, 1896, **9**, 89, 578.

[52] British Patent 20,879, 1898; *J.S.C.I.*, 1899, **18**, 128.

[53] Austrian Patent 1,448, 1900; Hungarian Patent 15,489, 1899.

In another method for the preparation of sulphonic acids, Petroff[58] first diluted acid sludge with an equal part of water and heated the mixture in an autoclave for 3 to 4 hours at 20 atmospheres.[59] The oily layer was then distilled and the fractions were sulphonated. In related processes for the recovery of sulphonated materials from acid sludge, temperatures of 75° to 120° C.[60] and 160° to 180° C.[61] are used.

Oil-soluble sulphonic acids can be isolated by treating the sulphonated oil with an aqueous solution of acetic acid or one of its water-soluble esters.[62]

For the recovery of sulphonic acids of high molecular weight Petroff[63] has also suggested adsorbing them from solution on porous cellulose or wood flour, which is subsequently dried. From this the sulphonic acids can be extracted with benzene, alcohol, or other solvents.[64]

Sodium salts of organic sulphonic acids, which result on boiling the crude sulphonic acids with sodium chloride solution, can be purified, according to Twitchell,[65] by salting out the simultaneously formed sodium sulphate and extracting the free unsulphonated mineral oils with organic solvents. Petroff[66] treated the aqueous solution of sulphonic acids in alkali with gasoline, to remove the hydrocarbons, and salted out the dissolved sulphonates with sodium chloride.

Recovery of sulphonic acids from acid sludge in the form of their calcium

[54] The manufacture of sulphonic acids from petrolatum is described by Montag, *Azerb. Neft. Khoz.*, 1927, No. 1, 48; *Chem. Abs.*, 1927, **21**, 3738; Vlasenko, *Azerb. Neft. Khoz.*, 1927, **10**, 86; *Chem. Abs.*, 1927, **21**, 497; Tilitschejev and Dumiskaja, *Neft. Khoz.*, 1926, **11**, 738; *Chem. Zentr.*, 1927, **1**, 2380; *Chem. Abs.*, 1928, **22**, 3286; Budrewicz, *Przemysl Chem.*, 1920, **4**, 63; *Chem. Zentr.*, 1920, **4**, 448; *J.S.C.I.*, 1920, **39**, 740A; Razderishin and Dennemark, *Neft. Khoz.*, 1931, **20**, 95; *Chem. Abs.*, 1932, **26**, 4452.

[55] Russian Patent 428, 1911, 1924; *Chem. Abs.*. 1928, **22**, 4243; *ibid.*, 1933, **27**, 1501; Russian Patent 508, 1913, 1924; *Chem. Abs.*, 1928, **22**, 4131; *ibid.*, 1933, **27**, 1501; French Patent 448,207, 1912; *Chem. Abs.*, 1913, **7**, 2112; German Patent 271,433, 1912; *Chem. Abs.*, 1914, **8**, 2481; British Patent 19,676, 1912; *Chem. Abs.*, 1914, **8**, 571; U. S. Patent 1,087,888, Feb. 17, 1914; *Chem. Abs.*, 1914, **8**, 1344; U. S. Patent 1,233,700, July 17, 1917; *Chem. Abs.*, 1917, **11**, 2609.

[56] Petroff, U. S. Patent 1,087,888, Feb. 17, 1914; *Chem. Abs.*, 1914, **8**, 1344; French Patent 448,207, 1912; *J.S.C.I.*, 1913, **32**, 415. See also Russian Patent 460, 1912, 1924; *Chem. Abs.*, 1928, **22**, 4243; *ibid.*, 1933, **27**, 1497; *cf.* Montag, Russian Patent 803,428; *Chem. Abs.*, 1927, **21**, 3738.

[57] The disinfectant properties of petroleum sulphonic acids are discussed by Petroff in Russian Patent 2,838.

[58] Russian Patent 1,447, 1924; *Chem. Abs.*, 1928, **22**. 4243.

[59] *Cf.* Berguer, Russian Patent 10,416; assigned to Nobel Bros.; described by Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, 1932, 459.

[60] Mann and Holmes, U. S. Patent 1,838,030, Dec. 22, 1931; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1932, **26**, 1429.

[61] Burgess and Buc, U. S. Patent 1,767,344, June 24, 1930; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, **24**, 4384.

[62] Schestakoff, U. S. Patent 1,706,940, Mar. 26, 1929; *Chem. Abs.*, 1929, **23**, 2290; French Patent 622,693, 1927; British Patent 247,940, 1925; *Chem. Abs.*, 1927, **21**, 593; German Patent 444,326.

[63] U. S. Patent 1,766,304, June 24, 1930; *Chem. Abs.*, 1930, **24**, 4053; British Patent 284,859, 1927; *Chem. Abs.*, 1928, **22**, 4539; German Patent 517,156, 1927; *Chem. Abs.*, 1931, **25**, 2156; French Patent 628,129, 1927.

[64] The manufacture and uses of "kontakt" is described by Petroff, *Azer. Neft. Khoz.*, 1927, No. 12, 48; *Chem. Abs.*, 1928, **22**, 1246; see also *Oil and Fat Ind.* (*Russia*), 1926, (6) 25; (7 and 8) 21; *Chem. Zentr.*, 1927, **1**, 3156; *Chem. Abs.*, 1928, **22**, 3544; Petroff and Rabinowitsch, "Nieftianize Sulfokisloty," Naucz. Chem. Techn. Izd., Leningrad, 1929.

[65] Swiss Patent 72,380, 1916; *Chem. Abs.*, 1916, **10**, 2412; Swedish Patent 43,923, 1918; *Chem. Abs.*, 1919, **13**. 378.

[66] Russian Patent 1,449, 1923; *Chem. Abs.*, 1933, **27**, 1497.

salts was proposed by Divine.[67] He allowed the acid sludge to stand with water for 8 to 12 hours. The lower layer, which consists of an aqueous solution of the sulphonic acids and sulphuric acid, is separated, neutralized with calcium hydroxide and the precipitated calcium sulphate is filtered off. The calcium sulphonates are precipitated from the filtrate by the addition of about 20 per cent of sodium or calcium chloride. The calcium sulphonate is a water-soluble, light yellow plastic material with a distinct aromatic odor. The use of this and similar products as detergents, fat-splitting reagents and for other purposes is discussed in a succeeding section of this chapter.

The recovery of sulphonic acids with calcium hydroxide has also been described by Pilat and Sereda.[68] By boiling the calcium sulphate precipitate with sodium carbonate, the insoluble calcium sulphonates are converted into their soluble sodium salts, which can be salted out of solution.

Divine [69] recommended the recovery of sulphonic acids by boiling the sludge with a solution of aluminum sulphate. The precipitate which forms is washed with water and from it the sulphonic acids are liberated with sulphuric acid. Similar methods have also been described by Taveau [70] for the separation of sulphonic acids during the treatment of petroleum acid sludge to obtain asphalts, and by Fischer and Reddish.[71] The latter investigators decomposed the aluminum sulphonates with sodium hydroxide, using phenolphthalein as indicator.

Sulphonic acids can be recovered from acid oil, which remains after tar has been removed from acid sludge, in the following manner: The acid oil is treated with alkaline solutions and alcohol. Sodium chloride, which is then added to the alkaline liquid, causes a separation into two layers, one of which contains about 30 per cent sodium sulphonate and 30 per cent mineral oil, together with salt and free alkali. Methyl alcohol, ethyl alcohol, acetone or other solvent miscible with water is added to the lower layer. The mineral oils thus precipitated are subsequently removed and the solvent evaporated. From the residue, the sulphonic acids are precipitated by the addition of inorganic acids.[72] These crude sulphonic acids can be purified by washing at about 60° C. with 40 to 50 per cent sulphuric acid.[73] However, the resulting sulphonic acids still contain about 5 per cent sulphuric acid, which can be removed by the addition of alcohol and neutralization with solid sodium carbonate.[74] The precipitated sodium sulphate is filtered or allowed to settle out and the solution is evaporated.

The following method was suggested by Happach.[75] The acid tar is dissolved or emulsified in water or an alkaline solution and subjected to fractional precipitation by the addition of sodium chloride or calcium chloride. Sufficient salt is added to precipitate the sulphones and neutral hydrocarbons but not the sulphonic acids. After separating the precipitated material, the bulk of the sulphonic acids is thrown down by the further addition of salt. The salts of the sulphonic acids thus obtained may be purified by solution in water and further fractional precipitation or by treatment with a solvent. The latter method of purification consists in extracting the sulphonic acids with water and treating the aqueous solution of sulphonic acids with a small proportion of methanol, ethanol, or acetone. Petroleum hydrocarbons separate and form an upper layer while sulphonic acids remain in solution.

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[67] U. S. Patent 1,301,662, Apr. 22, 1919; *Chem. Abs.*, 1919, **13**, 1924; U. S. Patent 1,303,779, May 13, 1919; assigned to Twitchell Process Co.; *Chem. Abs.*, 1919, **13**, 1924; Canadian Patents 192,486 and 192,487, 1919; *Chem. Abs.*, 1919, **13**, 2770; U. S. Patent 1,330,624, Feb. 10, 1920; *Chem. Abs.*, 1920, **14**, 1216. Twitchell Process Co., British Patent 127,159, 1918; *Chem. Abs.*, 1919, **13**, 2439; British Patents 143,682 and 143,683, 1919; *Chem. Abs.*, 1920, **14**, 2984.

[68] British Patent 343,530, 1929; *Brit. Chem. Abs.* **B**, 1931, 474; French Patent 694,236, 1930; *Chem. Abs.*, 1931, **25**, 1954.

[69] U. S. Patent 1,438,101, Dec. 5, 1922; *Chem. Abs.*, 1923, **17**, 894.

[70] U. S. Patent 1,271,387, July 2, 1918; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1918, **12**, 1925.

[71] U. S. Patent 1,734,369, Nov. 5, 1929; assigned to Twitchell Process Co.; *Brit. Chem. Abs.* **B**, 1930, 7.

[72] Oelwerke Stern-Sonneborn A.-G., German Patent 310,701, 1914; *J.S.C.I.*, 1922, **41**, 850A.

[73] Oelwerke Stern-Sonneborn A.-G., German Patent 350,299, 1915; *J.S.C.I.*, 1922, **41**, 676A; Wolff, U. S. Patent 1,428,197, Sept. 5, 1922; *Chem. Abs.*, 1922, **16**, 3666.

[74] Oelwerke Stern-Sonneborn A.-G., German Patent 385,222, 1915; *J.S.C.I.*, 1924, **43**, 411B; Wolff, U. S. Patent 1,240,523, Sept. 18, 1917; *Chem. Abs.*, 1917, **11**, 3427.

[75] German Patent 310,925, 1913; *J.S.C.I.*, 1919, **38**, 404A; addition to German Patent 264,785, 1913; both assigned to Sudfeldt and Co.; see also British Patent 148,579, 1920; *J.S.C.I.*, 1921, **40**, 74A.

Sulphonates can be removed from sulphonated petroleum oil by washing the oil with isopropyl alcohol, according to Robinson.[76] A similar method of recovering oil-soluble sulphonic acids produced in the manufacture of white petrolatum has been described by Cobb and Holmes.[77] For improving the color of the salts of oil-soluble sulphonates, Buc [78] heated them to above 150° C. in the presence of 3 per cent sodium hydroxide solution and purified them further with isopropyl alcohol. During evaporation of the isopropyl alcohol, from 1 to 10 per cent of a sodium salt of a weak organic acid, such as sodium resinate, can be added to prevent darkening.[79]

The treatment of the heavier fractions of petroleum for the production of highly refined products, yields not only the ordinary oil-soluble sulphonic acids known as "mahogany" acids [80] but also under certain conditions, acids which are insoluble in oil but readily soluble in water, chloroform, alcohols, and benzene and sparingly soluble in carbon tetrachloride, carbon disulphide, xylene, naphtha and ether. To these latter acids the term "green" acids has been applied. The sludge from a mineral oil, for example, a lubricating stock from a Mid-Continent crude petroleum, which has been sulphonated by successive additions of fuming sulphuric acid, is subjected to the following treatments, by Humphreys, Rogers and Bransky,[81] for separation of the green acids: The sludge is first diluted with a medium heavy hydrocarbon oil. The mahogany acids remain in the resulting oil layer which is separated. The residual sludge is boiled with water, the diluted sulphuric acid settling at the bottom. The supernatant layer is neutralized with sodium carbonate and the remaining oil is extracted with naphtha. The oil-free sodium sulphonates (green acid salts) are then purified by washing with sulphuric acid or by extraction with alcohol.

Cushman and Doell,[82] to obtain mineral oil sulphonated soaps, subjected the oil resulting from a preliminary treatment with sulphuric acid to the further action of sulphuric acid of 97 per cent concentration. From this second sludge the sulphonated products are separated from the free sulphuric acid and are neutralized. The oil-soluble coloring substances which remain in the soap are extracted with benzene. Petroleum oils can be sulphonated by emulsification with concentrated sulphuric acid, according to Terry and Craig.[83] When water is added to this emulsion, stratification occurs and the free acids separate in the aqueous solution. Myers [84] used sulphuric acid containing 25 to 35 per cent free sulphur trioxide at 50° to 60° C. to obtain maximum yields of oil-soluble sulphonates from the refining of medicinal oils.

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[76] U. S. Patent 1,387,868, Aug. 16, 1921; see also Cobb, U. S. Patent 1,387,835, Aug. 16, 1921; both assigned to Standard Oil Co. of N. J.; *J.S.C.I.*, 1921, **40**, 728A.

[77] U. S. Patent 1,707,187, Mar. 26, 1929; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1929, 634.

[78] U. S. Patent 1,707,506, Apr. 2, 1929; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1929, **23**, 2567.

[79] Buc and Tate, U. S. Patent 1,811,535, June 23, 1931; Canadian Patent 301,507, 1930; both assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, **24**, 4145; *cf.* Lyubarski, Russian Patent 24,936, 1932; *Chem. Abs.*, 1932, **26**, 3661.

[80] As the extent of this Chapter bears evidence, the literature describes many processes for sulphonating mineral oils for the purpose of obtaining sulphonates, nevertheless the commercial preparation of sulphonated mineral oils is largely confined to the recovery of these sulphonates as by-products from the manufacture of white medicinal and technical mineral oils. In the various white oil processes, the mineral oil is treated with fuming sulphuric acid and the mixture is allowed to separate into two layers. The upper oil layer contains most of the oil-soluble sulphonic acids and the lower sludge layer contains all of the water-soluble sulphonic acids together with minor proportions of the oil-soluble sulphonic acids. The upper oil layer is washed with aqueous ethyl or isopropyl alcohol, which solvents remove the sulphonic oil-soluble (mahogany) acids, or the upper oil layer is neutralized with an alkali and the sulphonic acids are extracted with alcohols as the alkaline salts (mahogany salts). The water-soluble sulphonic acids (green acids) are recovered from the sludge by extraction with water and other solvents. The relatively small proportion of oil-soluble sulphonates present may be removed from the sludge by extraction with hydrocarbons.

[81] U. S. Patent 1,474,933, Nov. 20, 1923, assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1924, **18**, 584. See also Coleman and Coleman (U. S. Patent 1,892,650, Dec. 27, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 2294) for separation of water-soluble sludge acids from acid refining of petroleum.

[82] U. S. Patent 1,718,335, June 25, 1929, assigned to Standard Oil Co. of California; *Chem. Abs.*, 1929, **23**, 4059.

Various solvents have been proposed for the separation of sulphonated products from acid sludges and other residues. The use of alcohols has already been mentioned. Bennett, Murphy and Story [85] suggested a mixture of alcohol and benzene. Holmes [86] refined petrolatum-yielding material by treatment with fuming sulphuric acid at 170° C., the purified petrolatum being removed by dissolving it in naphtha or benzene.

Residues from the cracking of heavy oils, treated with concentrated sulphuric acid free from sulphur trioxide, yield sulphonic acids which Bestuzhev and Sakhanov [87] extracted with a solvent.

The unsulphonated oils may be separated from the sulphonated oils in acid sludges by distillation *in vacuo* with superheated steam.[88] Before distillation the acid tars can be neutralized with alkali.[89] The residue is then treated with a solution of alkali in an organic solvent, particularly alcohol. Unsulphonated constituents, which may still be present, separate and the solution can be clarified, evaporated and acidified to obtain the sulphonic acids.

The progressive sulphonation of waste oils (which remain after the refining of mineral oil distillates with liquid sulphur dioxide) using sulphuric acid of increasing concentration is described by Kirch.[90] The reaction can be carried out in the presence of carriers such as organic or inorganic acids, anhydrides or chlorides.[91] Baddiley and Chapman [92] also sulphonated mineral oil fractions, for example, Borneo petroleum refined with liquid sulphur dioxide or those from oil-cracking processes, which have an initial boiling point above 200° C.

Petroff and Shestakoff [93] observed that crude petroleum distillates, which were no longer susceptible to sulphonation, could be sulphonated if first subjected to dehydrogenation. The crude material was blown with air at 140° to 150° C. until about 5 per cent of acid bodies were formed. The oxidized oil was then treated with an equal part of concentrated sulphuric acid (specific gravity 1.82) at 60° to 70° C., about 35 per cent of sulphonic acid derivatives being obtained. Higburg and Reilly [94] vaporized and superheated distillates containing a sub-

[83] U. S. Patent 1,867,778, July 19, 1932, assigned to Standard Oil Co. of California; *Chem. Abs.*, 1932, **26**, 5200.

[84] U. S. Patent 1,824,615, Sept. 22, 1931; assigned to Twitchell Process Co.; *Chem. Abs.*, 1932, **26**, 294.

[85] U. S. Patent 1,568,261, Jan. 5, 1926; *Brit. Chem. Abs.* **B**, 1926, 231.

[86] U. S. Patent 1,733,597, Oct. 29, 1929; *Chem. Abs.*, 1930, **24**, 495; *cf.* Cobb and and Holmes, U. S. Patent 1,707,187, Mar. 26, 1929; *Chem. Abs.*, 1929, **23**, 2290; both patents assigned to Standard Oil Development Co.

[87] Russian Patent 29,699, 1928; *Chem. Abs.*, 1931, **25**, 1069.

[88] Gelbke, German Patent 426,947, 1923; assigned to Sudfeldt and Co.; *Brit. Chem. Abs.* **B**, 1926, 526.

[89] Gelbke, German Patent 510,303, 1923; assigned to Sudfeldt and Co.; *Chem. Abs.*, 1931, **25**, 1069.

[90] German Patent 545,968, 1929; assigned to Chemische Fabrik Pott and Co.; *Chem. Abs.*, 1932, **26**, 3681.

[91] Kirch, German Patent 546,943, 1929; addn. to 545,968; assigned to Chemische Fabrik Pott and Co.; *Chem. Abs.*, 1932, **26**, 3681.

[92] British Patent 279,990, 1926; assigned to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1928, **22**, 3042; *cf.* U. S. Patents 1,836,428 to 1,836,431, Dec. 15, 1931; assigned to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1932, **26**, 1403; British Dyestuffs Corp., Ltd., French Patent 637,848, 1927; *Chem. Abs.*, 1929, **23**, 490.

[93] U. S. Patent 1,761,744, June 3, 1930; *Chem. Abs.*, 1930, **24**, 3638; German Patent 456,855, 1925.

[94] U. S. Patent 1,901,872, March 21, 1933; *Chem. Abs.*, 1933, **27**, 3321.

stantial amount of sulphonatable residue to convert a large part of the unsulphonatable constituents into sulphonatable products and gases.

Purification and deodorization of petroleum oils and naphtha by treatment with a sulphonating agent in the presence of about 5 to 15 per cent of stearic, oleic or other fatty acids of high molecular weight, has also been proposed by Petroff.[95]

Fischer and Reddish[96] purified neutralized mahogany acids, containing oil, by drying and mixing them with an aqueous solvent, for example, 75 per cent alcohol, saturated with sodium carbonate or other water-soluble salts. The sulphonates were concentrated thus in the upper layer and were recovered by decantation and evaporation of the solvent. A relatively homogeneous suspension of the sulphonates and entrained oil can be formed in an aqueous medium.[97] The separation of oil and sulphonates can be effected from this by centrifuging. Extraction of oil-soluble sulphonates with alcohol from lubricating oil stocks which have been treated with 5 to 10 per cent by weight of oleum for the preparation of medicinal white oils has been used by Reddish and Myers.[98] The alcoholic extract of the sulphonic acids was neutralized and evaporated and yielded pure sulphonic acids free from alcohol and water.

The constituents of high-boiling mineral oils which are insoluble in liquid sulphur dioxide have been sulphonated at normal temperature by Limburg[99] to obtain water-soluble sulphonic acids, the calcium salts of which are soluble in water and calcium chloride solution. Sulphonic acids, the calcium salts of which are insoluble in water, can be treated further with concentrated or fuming sulphuric acid to obtain sulphonic acids which yield soluble calcium salts.[100]

The purification of these sulphonic acids can be accomplished in a number of ways. Thus, the sulphonic acids can be purified by the addition of a volatile electrolyte, for example, ammonia or hydrogen chloride, to an aqueous solution of the crude acids.[101] Alternatively, to the aqueous solution can be added tar oil sufficient in quantity to separate with all the sulphonic acids.[102] The residual aqueous solution is withdrawn and the tar oil is distilled from the purified products. To remove oil-soluble sulphonated products formed in refining, alcoholic alkali has also been used. Accordingly, the sulphonated residue is made neutral or feebly alkaline and is then treated with dilute alcohol.[103] Eichwald[104] purified sulphonic acids by dissolving them in amyl alcohol or an alcohol practically insoluble in water and washed this solution with water. Ammonia or volatile organic bases such as propylamine, aniline, or cyclohexylamine, which do not form water-insoluble compounds with the impurities, have also been proposed for the precipitation of the sulphonic acid salts from aqueous solutions.[105]

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[95] U. S. Patent 1,766,305, June 24, 1930; *Chem. Abs.*, 1930, **24**, 4147; British Patent 291,823, 1927; *Chem. Abs.*, 1929, **23**, 1260; German Patent 517,197, 1927; *Chem. Abs.*, 1931, **25**, 2280.

[96] U. S. Patent 1,703,838, Feb. 26, 1929; *Chem. Abs.*, 1929, **23**, 2057; *cf.* U. S. Patent 1,731,716, Oct. 15, 1929; *Chem. Abs.*, 1930, **24**, 235; both patents assigned to Twitchell Process Co.

[97] Heckel and Reddish, U. S. Patent 1,775,622, Sept. 9, 1930; assigned to Twitchell Process Co.; *Chem. Abs.*, 1930, **24**, 5149.

[98] British Patent 347,164, 1929; *Chem. Abs.*, 1932, **26**, 1768; French Patent 679,210, 1929; *Chem. Abs.*, 1930, **24**, 3897.

[99] U. S. Patent 1,895,195, Jan. 24, 1933; assigned to Flintkote Corp.; *Chem. Abs.*, 1933, **27**, 2572; German Patent 531,157, 1928; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1931, **25**, 5588; French Patent 663,503, 1928; *Chem. Abs.*, 1930, **24**, 670. See also Langedijk, German Patent 528,583, 1929; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1931, **25**, 5176; French Patent 684,992, 1929; *Chem. Abs.*, 1930, **24**, 5441.

[100] Bataafsche Petroleum Maatschappij, German Patent 536,273, 1930; *Chem. Abs.*, 1932, **26**, 1434; French Patent 698,536, 1930; *Chem. Abs.*, 1931, **25**, 3015.

[101] Bataafsche Petroleum Maatschappij, British Patent 300,264, 1927; *Chem. Abs.*, 1929, **23**, 3479; French Patent 663,314, 1928; *Chem. Abs.*, 1930, **24**, 629.

[102] Bataafsche Petroleum Maatschappij, French Patent 694,578, 1930; *Chem. Abs.*, 1931, **25**, 1842.

[103] Bataafsche Petroleum Maatschappij, German Patent 539,270, 1930; *Chem. Abs.*, 1932, **26**, 1623; Dutch Patent 28,002, 1932; *Chem. Abs.*, 1933, **27**, 1363; *cf.* Voogt, U. S. Patent 1,901,383, March 14, 1933; assigned to Shell Development Co.; *Chem. Abs.*, 1933, **27**, 3069.

[104] U. S. Patent 1,868,596, July 26, 1932; assigned to Flintkote Corp.; *Chem. Abs.*, 1932, **26**, 5313.

A wide variety of hydrocarbon materials have been sulphonated by the I. G. Farbenindustrie A.-G. to produce wetting, cleansing and dispersing agents. Only a few of these will be mentioned. Chlorosulphonic acid has been recommended for the sulphonation of solar, yellow, gas, paraffin and other mineral oils and hydrocarbons obtainable from brown-coal or shale-tar.[106] Sulphonation of the oils together with aromatic or hydroaromatic hydrocarbons was proposed by Marx, Broderson and Bittner.[107] Oxidation products of paraffin waxes can also be sulphonated with oleum or chlorosulphonic acid to give emulsifying and wetting agents.[108] Fats or oils which contain more than 8 carbon atoms, especially mineral lubricating fractions, may be sulphonated at —12° to —15° C. with sulphur trioxide, oleum, or chlorosulphonic acid dissolved in liquid sulphur dioxide.[109] Products of the destructive oxidation of non-aromatic hydrocarbons or further products obtained from these by catalytic reduction, dehydration or decarboxylation can be treated with sulphur trioxide at 20° to 40° C. to obtain wetting agents.[110] Wetting agents have also been prepared by sulphonation of olefins.[111]

A large number of halogen-substituted sulphonic acids have been described which are made, in general, by treating aliphatic, aromatic, or hydroaromatic compounds with sulphuric acid and halogen derivatives of acids, such as chlorosulphonic acid.[112] These materials can be used as protective agents for wool, silk, rayon, cotton, linen and similar fibers in washing, fulling, carbonizing, scouring, steeping, bleaching and dyeing.

Oils resembling Turkey-red oils have been prepared by treating naphthenic acids or their esters with reducing agents followed by sulphonation,[113] for example, with chlorosulphonic acid at 40° C. Arylamino-derivatives which have been prepared by condensing naphthenic acids with aromatic amines have also been sulphonated.[114] The sulphonic acid group in this reaction enters the aromatic ring. Mineral oil sulphonates can also be condensed with isopropyl or butyl alcohols, according to Baddiley and Chapman,[115] to yield emulsifying agents for dyes. The reaction is conveniently conducted at a temperature of 65° C. or lower and chlorosulphonic acid may be employed as the sulphonating agent.[116]

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[105] Limburg, German Patent 551,425, 1929; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, **26**, 4347; U. S. Patent 1,903,466, April 11, 1933; assigned to Flintkote Corp.; *Chem. Abs.*, 1933, **27**, 3224.

[106] I. G. Farbenindustrie A.-G., British Patent 267,924, 1926; *Chem. Abs.*, 1928, **22**, 1233; British Patent 271,071, 1926; *Chem. Abs.*, 1928, **22**, 1659; British Patent 269,942, 1926; *Chem. Abs.*, 1928, **22**, 1419; British Patent 272,967, 1926; *Chem. Abs.*, 1928, **22**, 1848; British Patent 267,534, 1926; *Chem. Abs.*, 1928, **22**, 1200; French Patent 632,633, 1927; *Chem. Abs.*, 1928, **22**, 3524; French Patent 632,155, 1927; *Chem. Abs.*, 1928, **22**, 3417; French Patent 633,661, 1927; *Chem. Abs.*, 1928, **22**, 3471.

[107] U. S. Patent 1,708,103, Apr. 9, 1929; assigned to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.* **B**, 1929, 466; I. G. Farbenindustrie A.-G., British Patent 271,474, 1926; *Chem. Abs.*, 1928, **22**, 1694.

[108] I. G. Farbenindustrie A.-G., British Patent 303,281, 1928; *Brit. Chem. Abs.* **B**, 1929, 197; French Patent 677,090, 1929; *Chem. Abs.*, 1930, **24**, 3092; *cf.* British Patent 309,875, 1927; *Brit. Chem. Abs.* **B**, 1929, 466; British Patent 324,031, 1928; *Brit. Chem. Abs.* **B**, 1930, 362; British Patent 343,524, 1929; *Chem. Abs.*, 1931, **25**, 4371; see also Chapter 45.

[109] I. G. Farbenindustrie A.-G., British Patent 346,945, 1930; *Brit. Chem. Abs.* **B**, 1931, 684.

[110] I. G. Farbenindustrie A.-G., British Patent 360,002, 1930; *Brit. Chem. Abs.* **B**, 1932, 221.

[111] This is discussed in section on sulphonation of olefins.

[112] Lindner and Russe, German Patent 539,551, 1928; *Chem. Abs.*, 1932, **26**, 2201; Lindner, German Patents 524,349, 1927; 527,214, 1929, addn. to 430,085; *Chem. Abs.*, 1931, **25**, 4720; patents assigned to Oranienburger Chemische Fabrik A.-G. Oranienburger Chemische Fabrik A.-G., British Patent 313,453, 1928; *Chem. Abs.*, 1930, **24**, 1230; British Patent 309,042, 1928; *Chem. Abs.*, 1930, **24**, 492; British Patent 275,267, 1926; *Chem. Abs.*, 1928, **22**, 2284; British Patent 283,864, 1927; *Chem. Abs.*, 1928, **22**, 4131; British Patent 288,126, 1927; *Chem. Abs.*, 1929, **23**, 536; British Patent 308,280, 1927; *Chem. Abs.*, 1930, **24**, 213; French Patent 676,336, 1929; *Chem. Abs.*, 1930, **24**, 2910; French Patent 640,617, 1925; French Patent 671,912, 1929; *Chem. Abs.*, 1930, **24**, 2284. Chemische Fabrik Milch A.-G., British Patent 289,841, 1927; *Chem. Abs.*, 1929, **23**, 848; British Patent 289,898, 1927; *Chem. Abs.*, 1929, **23**, 937; British Patent 289,863, 1927; *Chem. Abs.*, 1929, **23**, 937; French Patent 668,106, 1928; *Chem. Abs.*, 1930, **24**, 1523; French Patent 674,517, 1929; *Chem. Abs.*, 1930, **24**, 2561; all patents assigned to Oranienburger Chemische Fabrik A.-G.

[113] Deutsche Hydrierwerke A.-G., French Patent 701,256, 1930; *Chem. Abs.*, 1931, **25**, 3783; British Patent 359,116, 1930; *Brit. Chem. Abs.* **B**, 1932, 173.

[114] Soc. des produits chimiques et matières colorantes de Mulhouse, French Patent 711,952, 1930; *Chem. Abs.*, 1932, **26**, 1943.

Sulphonic acids (kontakt) which are satisfactory detergents have been obtained by Likhusin and Deĭ-Karkhanova[117] by treating kerosene distillates with gaseous sulphur trioxide. They found that the yield of acids was increased by the presence of higher-boiling fractions, best results being obtained with distillates with a boiling range up to 350° C.

Gilsonite distillates have been sulphonated to give products whose alkali salts exhibit detergent properties. These sulphonated hydrocarbons have been proposed also as catalysts for the hydrolysis of glycerides. Forrest, Hayden and Douthett[118] purified a gilsonite fraction with sulphuric acid and then treated it with fuming sulphuric acid. The product was a semi-drying viscous oily product, which when added to linseed oil promotes homogeneous drying.

PROPERTIES OF SULPHONIC ACIDS DERIVED FROM PETROLEUM

The sulphonic acids produced in the acid refining of the higher petroleum distillates are complex mixtures. They all undoubtedly contain at least one sulphonic acid group ($—SO_3H$) attached to a carbon atom but the structure of the hydrocarbon radical associated with this group in any particular class of sulphonic acids is not known. A number of rather sharply differentiated types of sulphonic acids of high molecular weight have been described. Sulphonated products derived from aromatic hydrocarbons, cycloparaffins, and polynuclear cycloparaffins can be formed from high-boiling oils. A considerable variation in properties and composition, however, is to be expected of petroleum sulphonic acids from various sources. It is even possible that some of the more reactive high molecular weight paraffins may undergo sulphonation with sufficient ease to yield sulphonic acids under the conditions employed in practice in the manufacture of white oils. It is probable that, in some cases at any rate, sulphonation is also accompanied by oxidation, so that the acids obtained contain either unsaturated linkages or hydroxyl groups or both.[119]

The mineral oil sulphonic acids (evidently formed by the action of oleum on petrolatum) investigated by Schestakoff and Rabinovitsch[120] were found to have the general formula $C_nH_{2n-12}SO_3$ and the average formula $C_{20}H_{27}SO_3H$. Two fractions which corresponded to $C_{17}H_{21}SO_3H$ and $C_{19}H_{25}SO_3H$ were separated. Their reactions revealed characteristics of aromatic compounds.

Von Pilat and Davidson,[121] from a careful examination of some sulphonic acids produced in acid refining, found them to correspond approximately to the formula $C_{24}H_{33}SO_3H$. These naphthenesulphonic acids, as they were called, did not lose their sulphonic acid group even on prolonged boiling with alcoholic alkali, and their barium salts possessed the rather exceptional property of being soluble in ether, from which they were precipitated by the addition of alcohol. The sodium salts exhibited high permanent foaming properties in aqueous solution which were retained even in fairly acid solutions.

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[115] British Patent 274,611, 1926; assigned to British Dyestuffs Corp., Ltd.; see also British Patent 384,367, 1926; *Chem. Abs.*, 1928, **22**, 4741; British Patent 286,197, 1926; *Chem. Abs.*, 1929, **23**, 249; British Patent 307,141, 1927; *Chem. Abs.*, 1929, **23**, 5285.

[116] Baddiley and Chapman, British Patent 311,885, 1928; assigned to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1930, **24**, 932; French Patent 635,264, 1927; *Chem. Abs.*, 1928, **22**, 4833; addn. Patent 36,744.

[117] *Azerb. Neft. Khoz.*, 1932, (11), 67; *Chem. Abs.*, 1933, **27**, 1494.

[118] U. S. Patent 1,459,328, June 19, 1923; *Chem. Abs.*, 1923, **17**, 2956; U. S. Patent 1,524,859, Feb. 3, 1925; *Chem. Abs.*, 1925, **19**, 1773; U. S. Patent 1,578,235, Mar. 23, 1926; *Chem. Abs.*, 1926, **20**, 1715 patents assigned to Barber Asphalt Co.

[119] The high solubility of some of the high molecular weight sulphonic acids may be due to the presence of hydroxyl groups produced by oxidation reactions (*cf.* Burkhardt, *J.C.S.*, 1930, 2387).

[120] *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 664; see also Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, 1932, 391.

[121] *Przemysl Chem.*, 1927, **11**, 141; *Chem. Abs.*, 1929, **23**, 2816.

Later, von Pilat and Davidson[122] investigated the technical naphthenesulphonic acids which separated during the alkali treatment of petroleum subsequent to acid refining. They obtained products which consisted of a thick, almost black liquid, containing 19 per cent of water and 6 to 8 per cent of ash. The crude material was soluble in water and possessed an acid value of about 25. Impurities in these acids were removed by extracting a slightly alkaline solution of them with limited amounts of ether. The residue was freed from the sodium salt solution, washed and dried at reduced pressure over phosphorus pentoxide when it formed a dark, gummy, hygroscopic mass. The molecular weight of this material was 400 to 401 by the boiling-point method, and 410 by titration, indicating that the acids were monobasic. They noticed that two series of salts could be derived from these acids, which they designated as α- and β-compounds, the latter being distinguished by their solubility in ether. The relationship of these compounds to one another has not yet been clearly defined.

The sulphonic acids formed in the refining of mineral oil were later distinguished by the solubility of their calcium salts. According to von Pilat, Sereda, and Szankowski,[123] three classes can be distinguished, characterized as follows:

α-Sulphonic Acids; found mainly in the acid sludge, but also partly in the oil-layer; calcium salts are insoluble in water and ether.

β-Sulphonic Acids; present principally in the oil phase but also occur in the acid sludge when oleum is used; calcium salts insoluble in water but soluble in ether.

γ-Sulphonic Acids; appear to remain in acid sludge only; calcium salts soluble in water but insoluble in ether.

The content of γ-acids depends on the source of the oil but their nature appears to be invariant, i.e., γ-acids from petroleum of different geographical origins are similar if not identical. From a variety of oils, two acids $C_9H_9SO_3H$ and $C_{19}H_{20}SO_3H$ were isolated as calcium salts. These were converted to sodium salts, methyl esters, sulphonyl chlorides and sulphonamides. Reduction of the sulphonyl chlorides gave substances similar to sulphinic acids or thiols, according to the conditions. Alkali fusions of the acids at 200° to 210° C. yielded phenolic compounds which formed red dyes with diazobenzene-p-sulphonic acid but gave no well-defined benzoyl derivatives. With acetyl chloride a substance $C_8H_8OOCCH_3$ was obtained from the phenolic compounds in one instance.

The oil-soluble sulphonic acids, for example, the technical mahogany acids exhibit a relatively high solubility in mineral oils and water. The mahogany acids are soluble in ether, chloroform and insoluble in amyl alcohol. Other sulphonic acids are the water-soluble green acids formed by exhaustive sulphonation of lubricant fractions. These green acids, described by Humphreys, Rogers and Bransky,[124] are readily soluble in either hot or cold water, difficultly soluble in oil, readily soluble in chloroform, aliphatic alcohols, and benzene, and somewhat sparingly soluble in carbon tetrachloride, carbon disulphide, xylene, naphtha, and ether. The combining weights of the green acids from lubricating oil sludge are approximately 360 and the acids, when anhydrous, are practically solid at ordinary temperature. They are strongly acid and may be titrated with methyl orange as an indicator.

[122] *Petroleum Z.*, 1928, **24**, 1559; *Brit. Chem. Abs.* **B**, 1929, 47.

[123] *Petroleum Z.*, 1933, **29** (3), 1; *Chem. Abs.*, 1933, **27**, 2287; *Brit. Chem. Abs.* **B**, 1933, 211. See also Neyman and Pilat, *Ind. Eng. Chem.*, 1934, **26**, 395.

[124] U. S. Patent 1,474,933, Nov. 20, 1923; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1924, **18**, 584.

Some of the sulphonic acids produced in the acid refining of heavier petroleum fractions exhibit colloidal characteristics. Although soluble in water to a considerable extent, these acids are usually readily displaced from their aqueous solutions by salts and mineral acids.[125]

Petroff[126] stated that the low molecular weight (350) oil-containing naphthenesulphonic acids are soluble in water in the presence of alkalies, acid and neutral salts to yield strongly foaming solutions, and the higher molecular weight (about 450) oil-containing acids, which possess colloidal characteristics, are soluble in water in the presence of ammonia, sodium carbonate, and sulphuric acid. When free from oil, the high molecular weight acids are soluble in water in the presence of most electrolytes.

The petroleum sulphonic acids form a large number of metallic salts some of which have attained considerable technical importance. According to Dobrjanski and Anurov, salts of the first group metals, except copper, are soluble in water while the beryllium, zinc, cadmium, and mercury salts are appreciably soluble in hot water.

USE OF MINERAL OIL SULPHONATES AS DETERGENTS

The mineral oil sulphonic acids were early proposed as fat-hydrolyzing agents and their salts as detergents, wetting and emulsifying agents. New applications for these materials have continually been found so that they now have a wide range of utility. Some of their uses will be discussed in the sections which follow.

Much interest has been centered about the detergent properties of these substances, probably because of the potentially large outlet for them in this field. Common fatty acid soaps cannot be used for all washing purposes (for example, in hard water). In attempting to find new and better washing materials a wide variety of products has been proposed.[127] Many of these have appeared on the market. A brief list of some of these newer detergents with their approximate composition and trade-mark names may serve to emphasize how great is the interest in these materials in fields other than that of petroleum.[128]

I. Soaps containing fat-dissolving chlorinated hydrocarbons embrace Lanadin, Hydraphthal, Terpuril, Cycloran, Sovental, and Prestabitol.

II. Alkylnaphthalenesulphonic acids include Nekal and Neomerpin.

III. Sodium salts of higher sulphated alcohols[129] are Avirol[130] and Gardinol. The word *hymolal,* derived from "high molecular alcohol," has been proposed[130a] to designate the C_{12} to C_{18} alcohols obtained by the reduction of fatty acids or esters or from other sources. The wetting and cleansing agents, such as those mentioned, which are principally alkali alkyl sulphates, can thus be called *hymolal salts.*

IV. A mineral oil sulphonic acid has been called Kontakt (noted earlier in this chapter).

V. Products derived from pyridine and other compounds include Tetracarnite.

VI. Salts of ester-like condensation products of ethionic acid and fatty acids are known under the general name of Igepons.[131]

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[125] Dobrjanski and Anurov, *Neft. Khoz.*, 1927, 13, 200; *Chem. Abs.*, 1928, 22, 1674.

[126] *Masloboino-Zhirovoe Djelo,* 1929, 1, 34; *Chem. Abs.*, 1930, 24, 4415.

[127] See van der Werth, "Neuere Sulfonierungsverfahren zur Herstellung von Dispergier-, Netz- und Waschmitteln," Allgemeiner Industrie-Verlag G.m.b.H., Berlin, 1932; Mullin and Stribling, *Textile Colorist*, 1929, 51, 367, 655, 727, 807; *Textile Recorder*, 1930, (571), 65; (572), 61; (573), 63.

[128] This list is reported by Landolt, *Melliand Textilber.*, 1928, 9, 759; *Chem. Abs.*, 1928, 22, 4830; other additions have been made from sources indicated.

[129] General articles on these sulphated higher alcohols are those by Killeffer, *Ind. Eng. Chem.*, 1933, 25, 138; Lederer, *Seifensieder-Ztg.*, 1932, 59, 13; Friedrichs, *Farben-Chemiker,* 1932, 3 (11), 413; Duncan, *Ind. Eng. Chem.*, 1934, 26, 24.

[130] Pomeranz, *Seifensieder-Ztg.*, 1931, 58, 760; *Chem. Abs.*, 1932, 26, 2612.

[130a] *Ind. Eng. Chem., News Ed.*, 1934, 12 (6), 98.

[131] Hueter, *Chem. Umschau Fette, Öle, Wachse Harze,* 1932, 39, 25; *Chem. Abs*, 1932, 26, 2611. Some of these are described in the section on sulphonation of olefins.

Petroff[131a] stated that the oil-free naphthenesulphonic acids and their neutral salts are superior in detergent properties to ordinary soaps and the oil-containing sulphonic acids (and neutral salts) are equal to soaps. The presence of free sulphuric acid, he reported, is without influence on the detergent power of the sulphonates. Petroff found that an increase in the molecular weight of the sulphonic acid resulted in a lowering of the detergent power and the solubility in water. Thus, for example, three acids of molecular weights 350, 400, and 450, respectively, had detergent powers in the ratio of 5:3:2.

The low molecular weight naphtha sulphonic acids were considered by Schaeffer[132] to be equal to soap flakes in the scouring of cotton goods. Attention has been drawn to the excellent emulsifying power of the alkali salts of naphthenesulphonic acids which renders them valuable as detergents and Schaeffer described a method of analysis of such substances in mixtures which contain mineral oils.

Because of the wide variety of products, considerable effort has been made to have some standard procedure for their evaluation. Methods for the testing and comparison of detergents have been described by Zhukov and Schestakoff,[133] Schaeffer,[134] Pantyukhov[135] and by the Reichsausschuss für Lieferbedingungen.[136] Provisional procedures for the standardization of detergents have been advanced by the Detergent Committee of the American Oil Chemists' Society.[137]

The alkali salts of most mineral oil sulphonic acids which have been described in the preceding section have been proposed as detergents. In the following section a few specific methods for the production of detergent compositions are mentioned.

A neutral detergent composition was made by Petroff[138] by treating an aqueous alcoholic solution of the sulphonic acids produced in refining mineral oils with a solution of alkali or ammonia. The solvent is distilled from the non-oily alkali-sulphonic acid compounds thus obtained. A washing composition was made by incorporating the polymerization products of drying or semi-drying oils and fats with the sulphonation products of petroleum naphtha or mineral oils.[139]

A detergent consisting of an alkali sulphonate extracted by water from acid sludge was used by Divine.[140] Reddish[141] proposed an oil-soluble sulphonate combined with a stable water-soluble amine such as triethanolamine. A mixture of oil-soluble and oil-insoluble mineral oil sulphonates, recovered from the oil and sludge layers, respectively, in refining petroleum fractions having a naphthenic base can be used as a detergent in acid, alkaline or hard water.[142] A liquid consisting of 99 per cent water and 1 per cent mineral oil sulphonates has been recommended as a wetting agent.[143] Carver,[144] for removing mineral oils from various surfaces, used a detergent comprising 25 per cent alkali metal mineral oil sulphonate, 25 per cent coconut oil soap and 50 per cent water. Wetting agents have been produced by treating bark-tanned leather waste with aqueous solutions of sulphonic acids or their salts to form plastic masses.[145]

[131a] *Masloboino-Zhirovoe Delo,* 1929, (1), 34; *Chem. Abs.,* 1930, 24, 4415. Statements concerning relative detergency are oftentimes misleading as testing methods and wash goods vary, giving rise to conflicting results. A strict comparison demands resort to tests of a standardized character to be made under uniform conditions. Since such information is lacking in most cases the author has to rely on data furnished by the investigator. Götte (*Kolloid-Ztg.,* 1933, 64, 327, 331; *Brit. Chem. Abs.* B, 1933, 973) observed that maximum detergency in an alkaline solution of the sodium salts of alkylsulphonic acids ranging from C_{12} to C_{18} is dependent on chain length. Maximum detergency is displaced in the direction of increasing chain length by rise of temperature and by increase in water hardness. Götte reported that, in alkaline solutions, the sulphonates which he examined had several times the detergent power of soaps but that the difference is less marked in neutral and acid solutions. Foaming is most evident at concentrations at which molecular aggregates form and does not bear any simple relation to detergency.

[132] *Chem. Umschau Fette, Oele, Wachse Harze,* 1931, 38, 131; *Chem. Abs.,* 1931, 25, 3861.

[133] *Chem. Ztg.,* 1911, 35, 1027; *Chem. Abs.,* 1911, 5, 3924.

[134] *Loc. cit.*

[135] *Masloboino-Zhirovoe Delo,* 1929, (2), 20; *Chem. Abs.,* 1930, 24, 4415.

[136] "Prüfverfahren für Seifen und seifenhaltize Waschmittel," RAL, Nr. 871A2, Beuth-Verlag G.m.b.H., Berlin, S14, 1931.

[137] Reports of this committee appear in *Soap,* 1930, 5 (11), 55; *Chem. Abs.,* 1930, 24, 4415; *Oil and Fat Industries,* 1931, 8 (11), 413; *Oil and Soap,* 1932, 9 (11), 260. Burkhardt and Falkman (*Oil and Fat Industries,* 1931, 8 (11), 416) made a comparison of various common soaps.

[138] U. S. Patent 1,196,274, Aug. 29, 1916; *Chem. Abs.,* 1916, 10, 2648; Russian Patent 4,300, 1924; *Chem. Abs.,* 1928, 22, 4789; British Patent 19,759, 1912; *Chem. Abs.,* 1914, 8, 589; British Patent 19,676, 1912; *Chem. Abs.,* 1914, 8, 571.

[139] Petroff, U. S. Patent 1,661,620, Mar. 6, 1928; *Chem. Abs.,* 1928, 22, 1447; Russian Patent 1,448, 1926, 1923; *Chem. Abs.,* 1928, 22, 3061; *ibid.,* 1933, 27, 1464; German Patent 484,129, 1925; *Chem. Abs.,* 1930, 24, 931.

[140] U. S. Patent 1,301,663, Apr. 22, 1919; *Chem. Abs.,* 1919, 13, 1925; U. S. Patent 1,493,111, May 6, 1924; assigned to Twitchell Process Co.; *Chem. Abs.,* 1924, 18, 2073; Canadian Patent 192,488, 1919; *Chem. Abs.,* 1919, 13, 2771; Twitchell Process Co., British Patent 143,681, 1919; *Chem. Abs.,* 1920, 14, 2984.

[141] U. S. Patent 1,780,144, Oct. 28, 1930; assigned to Twitchell Process Co.; *Chem. Abs.,* 1931, 25, 179.

Becker and Müller[146] suggested for use as wetting, emulsifying or foaming agents, water-soluble sulphonated polymerization products of the lower hydrocarbons (prepared by the action of strong condensing agents such as sulphuric acid or zinc chloride on alcohols with more than 3 carbon atoms or on cracking gases). The properties can be improved by pretreating the polymerization products with lower aliphatic acid anhydrides or chlorides or by carrying out the sulphonation in the presence of these compounds. Products with similar properties can also be prepared from α-naphthalenesulphonic acid and butylene,[147] and from the treatment of butyl alcohol with solvent naphtha (or tetrahydronaphthalene) and sulphonated fatty acids (or naphthenic acids).[148]

Alcohols, hydroxy acids, or other products of high molecular weight obtained by the oxidation of paraffin wax,[149] or by halogenation of wax and subsequent treatment with alkali give, on sulphonation, esters which form the basis of other compositions having detergent properties.[150] The detergent power of these sulphonated products is improved by the addition of sodium bisulphate, silicate, phosphate or other sodium, potassium, magnesium, or amine water-soluble salts of acids stronger than carbonic.

The salts of sulphonated derivatives of the partial oxidation products of petroleum hydrocarbons have been proposed by James[151] as cleansing agents.

Chatrov[152] sulphonated the hydroxy acids obtained from the oxidation of paraffin wax. The products dissolved only in sodium hydroxide solution and partly in sodium carbonate and carbon disulphide and emulsified with water. The most highly sulphonated acid was a good wetting agent, but was not a satisfactory substitute for soap.

[142] Twitchell Process Co.; British Patent 350,505, 1930; *Chem. Abs.*, 1932, **26**, 3121; French Patent 688,513, 1930; *Chem. Abs.*, 1931, **25**, 785.

[143] Twitchell Process Co., French Patent 688,511, 1930; *Chem. Abs.*, 1931, **25**, 785.

[144] U. S. Patent 1,767,345, June 24, 1930; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, **24**, 4384.

[145] Oranienburger Chemische Fabrik A.-G., British Patent 355,282, 1929; *Chem. Abs.*, 1932, **26**, 5713.

[146] German Patent 550,242, 1928; assigned to Chemische Fabrik Pott and Co.; *Chem. Abs.*, 1932, **26**, 4143.

[147] Chemische Fabrik Pott and Co., Swiss Patent 127,252, 1926; *Chem. Abs.*, 1929, **23**, 1228.

[148] Chemische Fabrik Pott and Co., British Patent 266,746, 1926; *Chem. Abs.*, 1928, **22**, 880.

[149] Sulphonation of these oxidized paraffin waxes was described by I. G. Farbenindustrie A.-G., British Patent 303,281, 1928; *Brit. Chem. Abs.* **B**, 1929, 197; British Patent 309,875, 1927; *Brit. Chem. Abs.* **B**, 1929, 466; British Patent 324,031, 1928; *Brit. Chem. Abs.* **B**, 1930, 362; British Patent 360,002, 1930; *Brit. Chem. Abs.* **B**, 1932, 221; British Patent 343,524, 1929; *Chem. Abs.*, 1931, **25**, 4371; British Patent 373,642, 1932; *Chem. Abs.*, 1933, **27**, 4116; British Patent 388,877, 1933. French Patent 677,090, 1929; *Chem. Abs.*, 1930, **24**, 3092; French Patent 714,000, 1931; *Chem. Abs.*, 1932, **26**, 1732; Jahrstorfer and Hummel, German Patent 578,405, 1933; *Chem. Abs.*, 1933, **27**, 4435; Luther, German Patent 577,428, 1933; *Chem. Abs.*, 1933, **27**, 4043; U. S. Patent 1,908,376, May 9, 1933; *Chem. Abs.*, 1933, **27**, 3841; U. S. Patent 1,909,295, May 16, 1933; all patents assigned to I. G. Farbenindustrie A.-G. *Cf.* Bertsch, German Patent 552,327, 1926; assigned to H. T. Böhme A.-G.; *Chem. Abs.*, 1932, **26**, 4494.

[150] I. G. Farbenindustrie A.-G., British Patent 352,989, 1930; *Brit. Chem. Abs.* **B**, 1931, 1090; French Patent 703,466, 1930; *Chem. Abs.*, 1931, **25**, 4414; French Patent 40,987, 1931; addition to 703,466; *Chem. Abs.*, 1933, **27**, 1524; *cf.* British Patent 344,829, 1929; *Chem. Abs.*, 1932, **26**, 267.

[151] U. S. Patent 1,753,516, April 8, 1930; *Chem. Abs.*, 1930, **24**, 2591. The sulphonation of oxidized oils is described by Inman, *Ind. Eng. Chem.*, 1929, **21**, 542; see also Chapter 45.

[152] *Rekonstr. Textil. Prom.*, 1932, **11** (4), 48; *Chem. Abs.*, 1933, **27**, 2305.

MINERAL OIL SULPHONIC ACIDS AS FAT-HYDROLYZING AGENTS

About 1900 Twitchell [153] observed that benzenestearosulphonic and other similar acids [154] had the property of splitting fats (when heated with them) into glycerol and fatty acids. Sulphonic acids of this class became known as Twitchell reagents.

Divine [155] noted that the sulphonic acids which he recovered from petroleum acid sludge [156] had similar properties and could be used for treating low-grade fats and oils in the manufacture of fatty acids and glycerol.[157] A product obtained by boiling petroleum acid sludge with aluminum sulphate (method of separating out the sulphonic acids [158]) was also proposed for this purpose by Divine.[159]

Petroff [160] also used sulphonated mineral oil products for the splitting of fats. The fatty acids obtained were said to be decolorized by exposure to a current of air.[161] Charcoal was suggested as a decolorizing substance.[162] For decomposing the emulsions formed in saponifying fats with Twitchell and other reagents, Petroff [163] recommended the addition of a small proportion of calcium sulphate and sulphuric acid.[164] Petroff and Schestakoff [165] also prepared sulpho-aromatic fatty acids for fat-splitting.

SULPHONATED MINERAL OILS IN EMULSIONS

The mineral oil sulphonic acids act as stabilizers of certain types of emulsions but on other dispersions they exert a coagulating effect.[165a] Budriewicz [166] states that in mineral oil refining the sulphonic acids form troublesome emulsions on contact with water. To break these, the sulphonic acids are usually extracted with dilute alcohol. In such a solvent the acids apparently form normal solutions, as do ordinary soaps, but in water they are in a colloidal condition.[167] Sulphonic acids from white oils find particular use as emulsifying agents.[168]

Petroff [169] used mineral oil sulphonic acids for emulsifying oils, paraffin, waxes, resins, and fats. For example, the substance to be dispersed is mixed with a small amount of the sulphonic acid and a volatile solvent, such as benzene. Petroff's "kontakt" has been used for emulsifying hydrocarbon oils prior to oxidation with chromic acid to produce aldehydes.[170]

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[153] *J.A.C.S.*, 1906, **28**, 196; *ibid.*, 1907, **29**, 566. U. S. Patent 1,082,662, Dec. 30, 1913; *Chem. Abs.*, 1914, **8**, 834; U. S. Patent 1,170,468, Feb. 1, 1916; *Chem. Abs.*, 1916, **10**, 979; Dutch Patent 1,360, 1916; *Chem. Abs.*, 1916, **10**, 3172; British Patent 4,741, 1898; *J.S.C.I.*, 1898, **17**, 588; British Patent 9,160, 1913; *Chem. Abs.*, 1914, **8**, 3379; French Patent 456,956, 1913; *Chem. Abs.*, 1914, **8**, 2273.

[154] The preparation of these compounds was described by Twitchell, *J.A.C.S.*, 1900, **22**, 22.

[155] U. S. Patent 1,319,027, Oct. 14, 1919; assigned to Twitchell Process Co.; *Chem. Abs.*, 1920, **14**, 135.

[156] See U. S. Patent 1,303,779, May 13, 1919; previously described in this chapter.

[157] A report of the application of these reagents from the Twitchell Process Co. Lab. appeared in *Z. Deut. Oel-Fett-Ind.*, 1921, **41**, 649; *Chem. Abs.*, 1927, **16**, 843.

[158] Product made according to U. S. Patent 1,438,101, previously described.

[159] U. S. Patent 1,495,891, May 27, 1924; assigned to Twitchell Process Co.; *Chem. Abs.*, 1924, **18**, 2804.

[160] U. S. Patent 1,079,437, Nov. 25, 1913; Russian Patent 500, 1911; *Chem. Abs.*, 1933, **27**, 1535; Russian Patent 1,521, 1914; *Chem. Abs.*, 1933, **27**, 1535; British Patent 19,676, 1912; *Chem. Abs.*, 1914, **8**, 571; see also British Patent 252,212, 1925; *Chem. Abs.*, 1927, **21**, 1557.

[161] Petroff and von Fischenko, French Patent 467,188, 1914; *J.S.C.I.*, 1914, **33**, 875.

[162] Petroff, British Patent 252,211, 1925; *Chem. Abs.*, 1927, **21**, 1557.

[163] British Patent 274,741, 1927; *Chem. Abs.*, 1928, **22**, 2284; German Patent 540,218, 1927; *Chem. Abs.*, 1932, **26**, 1818.

[164] Fat-splitting by naphthasulphonic acids has been described by Petroff, Dimakov, and Taksa (*Seifensieder-Ztg.*, 1927, **54**, 163, 182, 204, 221, 241, 261, 284; *Chem. Abs.*, 1927, **21**, 3758). Petroff and Pichugina also discussed the complete hydrolysis of fats (*Masloboino-Zhirovoe Delo*, 1929, (9), 53; *Chem. Abs.*, 1931, **25**, 1694).

[165] U. S. Patent 1,642,595, Sept. 13, 1927; *Chem. Abs.*, 1927, **21**, 3760; British Patent 281,896, 1927; *Chem. Abs.*, 1928, **22**, 3795.

[165a] See Neyman and Pilat (*Ind. Eng. Chem.*, 1934, 26, 395) for emulsifying characteristics of these acids.

[166] *Przemysl Chem.*, 1920, **4**, 63; *Chem. Abs.*, 1921, **15**, 2177; *J.S.C.I.*, 1920, **39**, 740A.

[167] Dobryanskii and Anurov, *Neft. Khoz.*, 1927, **13**, 200; *Chem. Abs.*, 1928, **22**, 1674.

[168] The theories of the formation of petroleum emulsions are reviewed by Kalichevsky and Stagner, "The Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933; Vuishetravski, *Aserb. Neft. Khoz.*, 1929 (8-9), 53; *Chem. Abs.*, 1930, **24**, 951.

[169] U. S. Patent 1,230,599, June 19, 1917; *Chem. Abs.*, 1917, **11**, 2284; *cf.* Twitchell Process Co., French Patent 722,752, 1931; *Chem. Abs.*, 1932, **26**, 4195.

Limburg[171] also used mineral oil sulphonic acids (such as those described in this chapter[172]) to produce stable emulsions. As an illustration, Panuco asphalt was heated to about 95° C. and a 5 per cent aqueous solution of the sodium salt of the sulphonic acid was added with stirring, giving a dispersion.

Sulphonated mineral oils of high molecular weight were proposed by Levin[173] as dispersing agents for rubber. Smith[174] and Douthett[175] made emulsions of asphalt and tars with alkali salts of petroleum sulphonic acids. Coggeshall[176] recovered oil from oil sands by circulating an aqueous liquid comprising a highly dispersed colloidal mixture including a hydrocarbon sulphonate through the sands.

In the treatment of petroleum distillates with acids and alkalies, Petroff[177] prevented the formation of emulsions which carry off untreated hydrocarbons by washing the distillate with alcohol or acetone after the acid treatment. For breaking emulsions of petroleum and water, Rogers[178] proposed sodium and Fischer and Reddish suggested the use of sodium[179] or aluminum[180] salts of mineral oil sulphonates and pitch. Reddish[181] proposed the use of mineral oil sulphonates together with triethanolamine or other alkylolamines. Similar treatments of emulsions to effect their resolution have been described by Fischer and Reddish,[182] Heckel and Reddish,[183] Peirce and Reddish,[184] Myers,[185] Peirce and Myers,[186] de Groote and Monson,[187] and Mirzoyan, Romashenke and Fyurst.[188]

The sulphonic acids recovered from acid sludge by Taveau[189] have been recommended by Kennedy[190] for washing petroleum oils in refining operations to prevent emulsification. Burgess[191] also used sulphonic acids from acid sludge to break emulsions. In refining cracked gasoline stocks, Lachman[192] brought the vaporized hydrocarbon oil into contact with aqueous solutions of zinc,[193] copper, cadmium, mercury, iron, chromium, manganese, aluminum, nickel or cobalt salts of sulphonic acids and condensed the vapor.

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[170] Strunnikov and Seryakov, Russian Patent 29,839, 1927; *Chem. Abs.*, 1933, 27, 4241.

[171] German Patent 542,634, 1928; *Chem. Abs.*, 1932, 26, 3082; German Patent 536,912, 1928; *Chem. Abs.*, 1932, 26, 1435; Dutch Patent 23,111, 1930; *Chem. Abs.*, 1931, 25, 1645; British Patent 291,393, 1928; *Chem. Abs.*, 1929, 23, 1262; British Patent 300,574, 1927; *Chem. Abs.*, 1929, 23, 4061; French Patent 655,044, 1928; *Chem. Abs.*, 1929, 23, 3806; French Patent 35,865, 1928; addn. to 655,044; *Chem. Abs.*, 1930, 24, 4146; all patents assigned to Bataafsche Petroleum Maatschappij.

[172] Limburg, German Patent 531,157, 1928; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1931, 25. 5588.

[173] Canadian Patent 330,016, 1933; *Chem. Abs.*, 1933, 27, 2340.

[174] U. S. Patent 1,888,295, Nov. 22, 1932; assigned to Barber Asphalt Co., *Chem. Abs.*, 1933, 27, 1503.

[175] U. S. Patent 1,905,630, April 25, 1933; assigned to Barber Asphalt Co.; *Chem. Abs.*, 1933, 27, 3600.

[176] U. S. Patent 1,822,271, Aug. 8, 1931; *Brit. Chem. Abs.* B, 1932, 587.

[177] French Patent 448,207, 1912; *Chem. Abs.*, 1913, 7, 2112; German Patent 271,433, 1912; *Chem. Abs.*, 1914, 8, 2481.

[178] U. S. Patent 1,299,385, Apr. 1, 1919; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1919, 13, 1761.

[179] U. S. Patents 1,727,164 and 1,727,165, Sept. 3, 1929; assigned to Kontol Co.; *Chem. Abs.*, 1929, 23, 5312.

[180] U. S. Patent 1,710,159, Apr. 23, 1929; assigned to Kontol Co.; *Chem. Abs.*, 1929, 23, 2818.

[181] U. S. Patent 1,747,987, Feb. 18, 1930; assigned to Kontol Co.; *Chem. Abs.*, 1930, 24, 1734.

[182] U. S. Patent 1,734,369, Nov. 5, 1929; assigned to Twitchell Process Co.; *Chem. Abs.*, 1930, 24, 495.

[183] U. S. Patent 1,775,622, Sept. 9, 1930; *Chem. Abs.*, 1930, 24, 5149; U. S. Patent 1,872,286, Aug. 16, 1932; *Chem. Abs.*, 1932, 26, 6114; both patents assigned to Kontol Co.

[184] U. S. Patent 1,872,333, Aug. 16, 1932; assigned to Kontol Co.; *Chem. Abs.*, 1932, 26, 6114.

[185] U. S. Patent 1,837,130, Dec. 15, 1931; assigned to Kontol Co.; *Chem. Abs.*, 1932, 26, 1109.

[186] U. S. Patent 1,882,444, Oct. 11, 1932; assigned to Twitchell Process Co.; *Brit. Chem. Abs.* B, 1933, 695.

[187] U. S. Patents 1,766,057 to 1,766,065 and 1,766,112, June 24, 1930; assigned to Wm. S. Barnickel and Co.; *Chem. Abs.*, 1930, 24, 4145.

[188] Russian Patent 27,985, 1931; *Chem. Abs.*, 1933, 27, 3326.

[189] U. S. Patent 1,271,387, July 2, 1918; assigned to Atlantic Refining Co.; *J.S.C.I.*, 1918, 37, 539A.

[190] U. S. Patent 1,439,171, Dec. 19, 1922; assigned to Atlantic Refining Co.; *Chem. Abs.*, 1923, 17, 874.

[191] U. S. Patent 1,668,941, May 8, 1928; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1928, 22, 2268; Canadian Patent 269,105, 1927; *Chem. Abs.*, 1927, 21, 2382; *cf.* U. S. Patent 1,681,895, Aug. 21, 1928; *Chem. Abs.*, 1928, 22, 3984.

The reaction products from the sulphonation of mineral oils, which form colloidal suspensions with water, have been proposed by Moser[194] to bring about the separation of petroleum emulsions. Acid resins formed in the refining of light mineral oil fractions with sulphuric acid have also been suggested for the refining of heavy mineral oil fractions with sulphuric acid.[195] Canfield[196] suggested a mixture of a hydrocarbon-substituted derivative of a polycyclic sulphoaromatic compound, isopropylnaphthalenesulphonic acid,[197] for example, chlorobenzene, water, and a phenol, for treatment of wet petroleum oils. Derivatives of aromatic hydrocarbons have also been used for breaking petroleum emulsions.[198]

Mineral oil sulphonic acids have been suggested by Staegemann[199] for use as precipitants for proteins in acid solutions, such as from sewage and raw sugar juices.

SULPHONATED MINERAL OILS IN INSECTICIDES

A number of sulphonated mineral oil compounds have been used in sprays for killing insects. These will have brief mention here.

An insecticide containing a sulphonated petroleum and an alkylated sulphonated petroleum, particularly a sulphonated petroleum condensed with isopropyl alcohol has been suggested by Baddiley and Chapman.[200]

A basis for an insect spray has been obtained by treatment of a petroleum tar acid fraction boiling between 50° and 200° C. with sodium hydroxide and sodium plumbite.[201]

An insect-repellent mixture made by Grant[202] consists of a nicotine compound, a petroleum sulphonic acid, petroleum white oil and soap and water as an emulsifying agent. A sulphonated mineral oil treated with citric or other hydroxy-acid or a polyhydric alcohol, such as glycerol, in the presence of copper sulphate and an alkali is the basis of another insecticide.[203] Sullivan and Adams[204] used a composition of the following typical formula as a contact or stomach poison for insects or as a fungicide: liquid glue 5, water 33.5, copper resinate 8, lead arsenate 9, sodium mineral oil sulphonate 1.5, and white oil 43 per cent.

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[192] U. S. Patents 1,826,138 to 1,826,147, Oct. 6, 1931; assigned to Richfield Oil Co. of California; *Chem. Abs.*, 1932, **26**, 589.

[193] *Cf.* Lachman, U. S. Patent 1,790,622, Jan. 27, 1931; *Chem. Abs.*, 1931, **25**, 1374; U. S. Patent 1,809,170, June 9, 1931; *Chem. Abs.*, 1931, **25**, 4395; both patents assigned to Richfield Oil Co. of California.

[194] U. S. Patent 1,788,684, Jan. 13, 1931; assigned to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1931, **25**, 1067.

[195] Neftyanoi Sektor pri Glawnom Uprawleni Topliwa pri Wysschem Sowete Narodnogo Chosjaistwa, German Patent 582,172, 1933; *Chem. Abs.*, 1933, **27**, 5181.

[196] U. S. Patent 1,858,186, May 10, 1932; assigned to Empire Oil and Refining Co.; *Brit. Chem. Abs.* **B**, 1933, 295.

[197] Preparation is discussed in Chapter 24.

[198] Wayne, U. S. Patent 1,919,871, July 25, 1933; *Chem. Abs.*, 1933, **27**, 4914; de Groote and Keiser, U. S. Patent 1,842,934, Jan. 26, 1932; assigned to Tretolite Co.; *Chem. Abs.*, 1932, **26**, 1763.

[199] U. S. Patent 1,847,023, Feb. 23, 1932; assigned to Daytol Co.; *Brit. Chem. Abs.* **B**, 1932, 1069. *Cf.* Similar use of tumenol sulphonic acids described later in this chapter.

[200] French Patent 640,736, 1927; assigned to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, **23**, 927.

[201] Piotrowski and Winkler, British Patent 309,718, 1928; assigned to Galicyjskie Towarzystwo Naftowe Galicja Soc. Anon.; *Chem. Abs.*, 1930, **24**, 719.

[202] U. S. Patent 1,877,851, Sept. 20, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 366.

[203] Soc. Anon. des mines d'Orbagnoux, French Patent 733,615, 1931; *Chem. Abs.*, 1933, **27**, 1083.

[204] U. S. Patent 1,800,114, Apr. 7, 1931; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1931, **25**, 3119; *cf.* U. S. Patent 1,830,969, Nov. 10, 1931; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1932, 745.

An emulsion comprising straw oil, sodium mineral oil sulphonates, soap and alcohol has been proposed by Lambert [205] as an insecticide. Bottrell [206] suggested the use of sulphonethylmethane together with glue, water, alcohol, oil of peppermint or sodium benzoate as a rodent-repellent or insecticide.

Sulphonated oxidation products of petroleum act as insecticide activators, according to Inman.[207] Nicotine sulphate, not fully effective alone, is usually employed in the proportion of 1 part to 800 with soap as a spreader. If, instead of soap, a sulphonated oxidized petroleum [208] is added, the concentration of nicotine can be reduced.[209]

The penetration and toxicities of petroleum sprays was determined by Young.[210] Apple and potato leaves partly soaked with oils of less than 6 per cent sulphonatable residue lived for 30 to 80 days. Oils of greater than 13 per cent sulphonatable residue killed the leaves in 7 to 14 days and were toxic if applied in 4 to 8 per cent emulsions. The effect of petroleum oils on the respiration of leaves has also been examined.[211]

Woodworth [212] discussed the efficiency of petroleum oils as insecticides. Smith [213] made a study of the oil-depositing qualities of oil-spray mixtures. The determination of unsulphonated residue in petroleum spray oils has been described by Graham.[214]

MINERAL OIL SULPHONIC ACIDS FOR TEXTILE TREATMENTS

Numerous substances are finding application in the various treatments to which textiles are subjected in their manufacture.[215] Such compounds are usually designated as "*textile reagents*" ("textile assistants" in translations from the German) and may be used in textile treatment in the following way:

1. As a wetting, penetrating, or cleansing agent, for example, for removing natural or artificial impurities from animal or vegetable fibers. Thus, it may be employed in aqueous solution for degumming silk or for removing sizes from textiles of various kinds, or to wash out oils added during various spinning operations.
2. For lubricating or protecting fibers during weaving, spinning, or knitting. In this way it functions as a softening agent. The compound may be used in aqueous solution or as an emulsifying agent for oils.
3. For dispersing or solubilizing dyes or coloring matters in the dyeing of textiles. The compound may simultaneously act as a penetrating agent in the process.

The natural impurities contained in vegetable and animal fibers have been eliminated by heating the fibers in an aqueous solution of mahogany sulphonates.[216]

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[205] U. S. Patent 1,785,451, Dec. 16, 1930; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1931, 776.

[206] U. S. Patent 1,871,949, Aug. 16, 1932; assigned to Repulso, Inc.; *Chem. Abs.*, 1932, **26**, 6083.

[207] *Ind. Eng. Chem.*, 1929, **21**, 542.

[208] For example, oxidized product described by James in U. S. Patent 1,697,653, Jan. 1, 1929; *Brit. Chem. Abs.* **B**, 1929, 425.

[209] Fulton and Inman, U. S. Patent 1,826,065, Oct. 6, 1931; *Chem. Abs.*, 1932, **26**, 555.

[210] *Phytopath.*, 1931, **21**, 130; *Brit. Chem. Abs.* **B**, 1931, 1113.

[211] Green and Johnson, *Plant Physiology*, 1931, **6**, 149; *Chem. Abs.*, 1931, **25**, 3692.

[212] *J. Econ. Entomol.*, 1930, **23**, 848; *Chem. Abs.*, 1931, **25**, 1623.

[213] *J. Econ. Entomol.*, 1931, **24**, 985; *Chem. Abs.*, 1932, **26**, 2271.

[214] *J. Assoc. Off. Agric. Chem.*, 1927, **10**, 124; *Brit. Chem. Abs.* **B**, 1927, 290.

[215] The application of sulphonated fatty oils in textile treatment is discussed by Kelly, *Am. Dyestuff Reptr.*, 1933, **22**, 214; *Chem. Abs.*, 1933, **27**, 3353; *Chem. Markets*, 1933, **32**, 423.

[216] Twitchell Process Co., British Patent 354,303, 1930; *Chem. Abs.*, 1932, **26**, 5434; French Patent 690,434, 1930; *Chem. Abs.*, 1931, **25**, 1103; French Patent 688,514, 1930; *Chem. Abs.*, 1931, **25**, 827; French Patents 688,516 and 688,517, 1930; *Chem. Abs.*, 1931, **25**, 829; German Patent 536,806, 1930; *Chem. Abs.*, 1932, **26**, 1137.

Silk[217] has been degummed and artificial silk fibers have been prepared for further textile processing in this manner.[218]

Textile oils which can be used for the protection of artificial silk threads and fibers during weaving and knitting have been prepared by mixing mahogany sulphonates and mineral oils extracted with oleum.[219] A textile oil consisting of a low-viscosity mineral oil, an alkali metal soap of a sulphonated mineral oil, oleic acid, and an antioxidant such as beta-naphthol, has been suggested by Sullivan.[220]

Products which are wetting and protective agents for textiles and leather have been obtained by Keller and Gofferjé[221] by the action of fuming sulphuric acid or other sulphonating agent on the material which results from the reaction of an alkali on a polyhalo-derivative of higher paraffin hydrocarbons, for example, a dichloro-derivative of hard paraffin.

MISCELLANEOUS USES OF MINERAL OIL SULPHONIC ACIDS

Mahogany sulphonates have been used to make dyes soluble,[222] for example, in the dyeing of cellulose acetate silk.[223] Oil-soluble dyes have been made from basic dyes such as Victoria green, Bismarck brown, and Malachite green, by treatment with an aqueous solution of an oil-soluble sulphonated petroleum.[224] The absorption of dyes by mineral oil emulsions, according to Vellinger and Hemmer,[225] is a function of the concentration of the coloring material and the p_{H} of the aqueous solution.

Heckel[226] employed mahogany sulphonates for the dispersion of pigments in inks made with an oily medium.

Mineral oil sulphonic acids have been suggested as inhibitors in sulphuric acid pickling baths by Fischer and Stegemeyer.[227] Similar inhibiting agents for pickling baths have been suggested by Chapman[228] and Voorhees.[229] A metal cleaning and pickling composition suggested by Corson and Lawrence[230] consists of a dilute non-oxidizing acid and a small amount of a sulphonated mineral oil similar to ichthyol.

Organic solvents in which are dispersed sulphonated mineral oils and water have been proposed as dry cleaning fluids.[231] Such mixtures remove water-soluble stains as well as those soluble in the organic solvent.

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[217] Myers and Stegemeyer, U. S. Patent 1,896,494, Feb. 7, 1933; assigned to Twitchell Process Co.; *Chem. Abs.*, 1933, 27, 2825; Twitchell Process Co., German Patent 534,742, 1930; *Chem. Abs.*, 1932, 26, 1136.

[218] Twitchell Process Co., German Patent 536,886, 1930; *Chem. Abs.*, 1932, 26, 1135.

[219] Twitchell Process Co., French Patents 688,512 and 688,515. 1930; *Chem. Abs.*, 1931, 25, 827, 829; British Patent 349,962, 1930; *Chem. Abs.*, 1932, 26, 2067; British Patent 354,297, 1930; *Chem. Abs.*, 1932, 26, 3938; Reddish, U. S. Patent 1,909,721, May 16, 1933; assigned to Twitchell Process Corp.; *Chem. Abs.*, 1933, 27, 3834.

[220] U. S. Patent 1,871,927, Aug. 16, 1932; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* B, 1933, 661; *cf.* Kinney, U. S. Patent 1,871,889, Aug. 16, 1932; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, 26, 6160.

[221] U. S. Patent 1,876,975, Sept. 13, 1932; assigned to General Aniline Works; *Chem. Abs.*, 1933, 27, 196.

[222] Twitchell Process Co., French Patent 690,505, 1930; *Chem. Abs.*, 1931, 25, 1090.

[223] Twitchell Process Co., British Patent 354,326, 1930; *Chem. Abs.*, 1932, 26, 5433.

[224] Buc, U. S. Patent 1,841,876, Jan. 19, 1932; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1933, 262.

[225] *Ann. combustible liquides*, 1930, 5, 295; *Chem. Abs.*, 1930, 24, 5988.

[226] British Patent 360,075, 1930; *Chem. Abs.*, 1933, 27, 615; U. S. Patent 1,906,961, May 2, 1933; assigned to Twitchell Process Co.; *Chem. Abs.*, 1933, 27, 3627; *cf.* British Patent 360,948, 1930; *Brit. Chem. Abs.* B, 1932, 234; *cf.* Singer, British Patent 109,270, 1917; *Chem. Abs.*, 1918, 12, 93.

[227] U. S. Patent 1,736,282, Nov. 19, 1929; assigned to Twitchell Process Co.; *Chem. Abs.*, 1930, 24, 585.

[228] U. S. Patent 1,836,445, Dec. 15, 1931; assigned to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1228; *cf.* Imperial Chemical Industries, Ltd., British Patent 346,162, 1930; *Chem. Abs.*, 1932, 26, 416.

[229] U. S. Patent 1,838,338, Dec. 29, 1931; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, 26, 1228.

[230] Canadian Patent 316,994, 1931; assigned to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1231.

Some attention has been paid in the past to the possibility of using acid sludge as a basis for the manufacture of varnishes and drying oils.[232] Zaloziecki [233] described the production of varnishes from acid sludge. Tarry matter is boiled with an equal volume of water, and neutralized with basic oxides, carbonates, or organic bases. The resulting reddish-brown mass is either dehydrated and dissolved in a cold mixture of strong alcohol and benzene, oil of turpentine or tar-oil, or dissolved directly in an equal volume of 50 per cent alcohol and benzene to give lacquers.

According to Buc, certain of the heavy metal salts of oil-soluble petroleum sulphonic acids may be used as driers, either alone or in combination with other driers. The oil-soluble sulphonic acids (particularly those from lubricating distillates) are first converted into their sodium salts, which are extracted subsequently with a solvent (e.g., 35 to 65 per cent aqueous ethyl alcohol) and freed from oil by treatment with 10 to 20 per cent of gasoline. The sodium sulphonates are then converted into their lead,[234] cobalt,[235] or manganese [236] salts and freed from insoluble material by solution in an organic solvent (e.g., a mixture of benzene and 75 per cent ethanol or isopropanol), the purified salts being used as driers. The calcium salt of an oil-soluble sulphonic acid has been used in varnishes, for example, one consisting of 50 to 90 per cent of a drying oil (linseed or tung oil), 5 to 25 per cent of resins and 5 to 25 per cent of calcium sulphonates.[237] The above mixture may be reduced to the desired consistency by the addition of sufficient thinner, such as turpentine. Metallic salts of oil-soluble sulphonic acids likewise have been used by others in paints.[238]

Rial [239] used neutralized sludge from the refining of asphalt-base crude oils for a color coat for cemented surfaces. Water-insoluble residues of acid sludges have been used as waterproofing ingredients in concretes, mortars, and in gypsum and Sorel cement compositions.[240]

Bolgár [241] obtained a rubber-like material for impregnating jute and similar fibers by boiling linseed or other drying oil at 180° to 200° C. with the residual sludge from acid mineral oil refining.

According to Johnson,[242] a lubricant adapted for use in the die-drawing of metals consists of the sodium salt of green sulphonic acid (water-soluble) obtained from lubricating oil sludge, tallow, and water, the materials being heated to 82° C. to effect a homogeneous mixture.

The preparation of similar lubricants for like purposes is described by

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[231] Twitchell Process Co., French Patent 724,081, 1931; *Chem. Abs.*, 1932, **26**, 4966; Reddish, British Patent 392,931, 1931; *Brit. Chem. Abs.* **B**. 1933, 622.

[232] For example, see Millochan, U. S. Patent 37,918, Mar. 17, 1863; previously discussed in this chapter.

[233] *Chem. Rev. Fett- u. Harz-Ind.*, 1898, **5** (2), 27; *J.S.C.I.*, 1898, **17**, 340.

[234] U. S. Patent 1,686,484, Sept. 16, 1927; *Chem. Abs.*, 1928, **23**, 4844; French Patent 659,825, 1928; *Chem. Abs.*, 1929, **23**, 5338; both patents assigned to Standard Oil Development Co.

[235] U. S. Patent 1,686,485, Sept. 16, 1927; *Chem. Abs.*, 1928, **23**, 4844; French Patent 659,823, 1928; *Chem. Abs.*, 1929, **23**, 5338; both patents assigned to Standard Oil Development Co.

[236] U. S. Patent 1,686,486, Sept. 16, 1927; *Chem. Abs.*, 1928, **23**, 4844; French Patent 659,824, 1928; *Chem. Abs.*, 1929, **23**, 5338; both patents assigned to Standard Oil Development Co.

[237] Buc, U. S. Patent 1,735,493, Nov. 12, 1929; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1930, **24**, 739.

[238] e.g., Bataafsche Petroleum Maatschappij, French Patent 684,992, 1929; *Chem. Abs.*, 1930, **24**, 5441; British Patent 355,430, 1930; *Chem. Abs.*, 1932, **26**, 4189.

[239] U. S. Patent 1,864,942, June 28, 1932; assigned to Richfield Oil Co. of California; *Brit. Chem. Abs.* **B**, 1933, 508.

[240] I. G. Farbenindustrie A.-G., British Patent 368,498, 1931; *Chem. Abs.*, 1933, **27**, 2277.

[241] U. S. Patent 1,842,857, Jan. 26, 1932; *Brit. Chem. Abs.* **B**, 1932, 1042.

[242] U. S. Patent 1,795,491, Mar. 10, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 1039.

Adams,[243] Arveson,[244] and Sharp.[245] Bransky[246] prepared a rust-preventative which comprised a mixture of montan or carnauba wax and an oil-soluble sulphonic acid (20 to 60 per cent), brought to required consistency by the addition of a hydrocarbon oil.

Becker[247] proposed as a lubricant a mixture of a petroleum lubricating oil, an alkali soap of a fatty acid such as sodium oleate and an oil-soluble alkali metal mineral oil sulphonate. The latter facilitates feeding of the lubricant by a wick. A similar mixture can be used for lubricating artificial silk fibers during spinning.[248]

For wood preservation, Hampton and Farrington[249] used a composition consisting of 85 per cent fuel oil and the product resulting from the neutralization of an acid sulphur oil of a petroleum distillate from pressure cracking.

A fine-cutting and fine-finishing grinding compound which contains alkali sulphonates admixed with coarse particles of soft abrasive and fine particles of hard abrasive has been proposed by McClaughry,[250] A typical mixture for such a purpose is 15 per cent mineral oil sulphonates, 15 per cent oil, 30 per cent petroleum, 30 per cent of silicon carbide (150 to 220-mesh), and 10 per cent of emery (80 to 100-mesh).

Moeller[251] obtained a tanning composition by heating mineral oil acid sludge with a quantity of hydrocarbon (naphthalene or anthracene) corresponding to the excess sulphuric acid present, in the presence of formaldehyde, until the mixture was completely soluble in water. The latter was subsequently treated with an excess of alkali. Nastukov[252] condensed crude oil or solvent naphtha with sulphuric acid and formaldehyde. This product is then neutralized, washed, oxidized with dilute nitric acid and dissolved in dilute alkali to give a tanning material.

Considerable interest has been exhibited in the use of mineral oil sulphonic acids for making plastic compositions.[253] One of the many ways which have been proposed is given by Petroff.[254] He condensed phenol and formaldehyde under reduced pressure in the presence of coal-tar or mineral oils; and emulsifying agents, such as high molecular weight sulphonic acids. A dielectric material has been prepared by Nastukov[255] from the condensation of 4 volumes of petroleum oil containing both saturated and unsaturated hydrocarbons first with at least 2 volumes of concentrated sulphuric acid and then with 1 volume of formaldehyde solution. A transparent and flexible product has been made by Heckel[256] from a mixture of gelatin, petrolatum, mahogany sulphonates and butyl cellosolve or other clarifier.

[243] U. S. Patents 1,871,939 and 1,871,940, Aug. 16, 1932; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* B, 1933, 538.

[244] U. S. Patents 1,871,941 and 1,871,942, Aug. 16, 1932; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* B, 1933, 538.

[245] U. S. Patent 1,789,054, Jan. 13, 1931; assigned to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* B, 1931, 847.

[246] U. S. Patent 1,795,993, Mar. 10, 1931; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1931, 1039.

[247] U. S. Patent 1,888,974, Nov. 29, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 1745.

[248] Becker and Stonaker, British Patent 277,637, 1927; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1929, 202.

[249] U. S. Patent 1,873,582, Aug. 23, 1932; assigned to Standard Oil Co. of California; *Brit. Chem. Abs.* B, 1933, 615.

[250] U. S. Patent 1,855,195, Apr. 26, 1932; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1933, 269.

[251] U. S. Patent 1,448,278, Mar. 13, 1923; *Chem. Abs.*, 1923, 17, 1902.

[252] U. S. Patent 1,806,910, May 26, 1931; *Brit. Chem. Abs.* B, 1932, 238.

[253] See Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York.

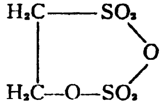
[254] British Patent 205,167, 1922; *Chem. Abs.*, 1924, 18, 911.

[255] U. S. Patent 1,827,538, Oct. 13, 1932; *Chem. Abs.*, 1932, 26, 540.

[256] U. S. Patent 1,902,304, March 21, 1933; assigned to Twitchell Process Co.; *Chem. Abs.*, 1933, 27, 3357.

Sulphonation of Olefins

The sulphonation reactions which have been reviewed previously in this chapter include those of the paraffins and cycloparaffins. Somewhat different products are obtained on the sulphonation of the olefins or sulphur-containing shale oils.

Some of the ways in which sulphuric acid can react with olefins have already been discussed in previous chapters. Faraday and Hennel,[257] as early as 1827, observed that ethylene was absorbed in sulphuric acid to form ethylsulphuric acid, which could be hydrolyzed to either ether or ethyl alcohol. Production of alcohols by such reactions is summarized in Chapters 13, 14 and 15. This absorption in sulphuric acid is also a convenient but not accurate method for the determination of the olefin content of gases and distillates (see Chapter 49). Higher olefins are polymerized by the action of sulphuric acid,[258] but ethylene is said to polymerize only when the acid contains a small proportion of such materials as copper and mercury sulphates.[259] These polymerization reactions are mentioned in Chapter 26. Of course, sulphuric acid also causes some oxidation of unsaturated hydrocarbons, this being evidenced by the sulphur dioxide odor on heating, but these reactions have received little attention.[260] Attention now is primarily directed to those reactions of ethylene which lead to the formation of carbyl sulphate  and its derivatives.

In 1837 Regnault[261] observed that, when ethylene and anhydrous sulphur trioxide were passed through a U-tube, a compound collected on the sides of the tube in radiated crystals[262] which melted at about 80° C. The compound was called carbyl sulphate. On dissolving in water, heat is evolved and ethionic acid, $HO_3S.C_2H_4.OSO_3H$ and some isethionic acid, $HO.C_2H_4.SO_3H$, are formed.

When a benzine fraction (boiling between 55° and 65° C.) was distilled in the presence of sulphuric acid and the distillate allowed to stand for 15 days, Boettger[263] noted the separation of fibrous crystals. The composition of these crystals corresponded to $C_5H_{10}SO_3$. They were insoluble in water or alcohol, but soluble in benzine.

According to Daimler and Platz,[264] ethionic acid and carbyl sulphate, or their homologues, may be produced by the action of sulphur trioxide or chlorosulphonic acid on aliphatic or hydroaromatic alcohols and olefins in the presence of liquid sulphur dioxide.[265] On hydrolysis, isethionic acid or its homologues is formed. Salts of ester-like condensation products of ethionic and fatty acids

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[257] *Poggendorff's Ann.*, 1827, **9**, 21; *ibid.*, 1828, **14**, 282; see Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1853, **8**, 168; see also Berthelot, *Ann.*, 1855, **94**, 78.

[258] For example, LeBel, *Compt. rend.*, 1871, **73**, 499; *Chem. Soc. Abs.*, 1871, **24**, 1025; see Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 268; Rossalimo, *J. Russ. Phys.-Chem. Soc.*, 1894, 1, 250; *Ber.*, 1894, **27**, Ref. 626; Brooks and Humphrey, *J.A.C.S.*, 1918, **40**, 822.

[259] Böeseken and Max, *Rec. trav. chim.*, 1929, **48**, 486; *Brit. Chem. Abs.* **A**, 1929, 674.

[260] See Graefe, *Z. angew. Chem.*, 1905, **39**, 1580.

[261] *Ann.*, 1837, **25**, 32; 1838, **69**, 168; *Annales de chimie et physique*, 1837, **65**, 98; *J. prt. Chem.*, 1837, **12**, 109. See Gmelin, "Handbook of Chemistry," translated by Watts, Cavendish Society, London, 1853, **8**, 168, 412.

[262] *Cf.* Magnus, *Ann.*, 1834, **6**, 163; *ibid.*, 1839, **32**, 251; *Poggendorff's Ann.*, 1938, **47**, 509; see Gmelin, *op. cit.*

[263] *Z. für Chemie*, 1866, **2**, 210.

[264] German Patent 550,572, 1930; *Chem. Abs.*, 1932, **26**, 4828; British Patent 378,895, 1931; *Brit. Chem. Abs.* **B**, 1932, 1072; French Patent 716,914, 1931; *Chem. Abs.*, 1932, **26**, 2751; all patents assigned to I. G. Farbenindustrie A.-G. U. S. Patent 1,913,794, June 13, 1933; *Chem. Abs.*, 1933, **27**, 4248.

[265] Merley and Spring (U. S. Patent 1,904,160, April 18, 1933; assigned to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 3224) prepared carbyl sulphate by reaction of ethylene and sulphur dioxide, and subsequently converted it to acetic acid.

(for example, Igepon) have received much attention as wetting and cleansing agents, especially in textile treatment. Reaction of hydroxyethanesulphonic acid with oleic acid chloride (oleyl chloride) at 80° to 100° C., yields ester-ethanesulphonic acids of the formula $HO_3S.C_2H_4.O.OC.R$, in which R represents an aliphatic hydrocarbon radical having more than 3 carbon atoms. According to Daimler and Platz,[266] these compounds have soap-like wetting and emulsifying properties. Halogenated ethanesulphonic acids can likewise be treated with salts of the higher fatty acids to give similar compounds. Ethionic acid or its anhydride (carbyl sulphate) can be used instead of hydroxyethanesulphonic acid—the fatty acids, their esters or chlorides, entering the molecule instead of sulphuric acid splitting out of the ethionic acid. If sulphuric acid is split out of the ethionic acid in some cases it may have a sulphonating action on the fatty acid but the properties of the resulting product are said to be unchanged.

Wetting agents can also be prepared by condensing butyl alcohol with hydroxyethane-sulphonic acid, beeswax with carbyl sulphate, or Japan wax with ethionic acid.[267]

The detergent properties of the sodium salts of the products resulting from the reaction of the chloride of oleic acid with ethionic acid are improved by the addition of sodium phosphate, zinc sulphate or magnesium sulphate. With such mixtures can be incorporated sodium bisulphite or other salts which have a bleaching action.[268]

1-Propanol-3-sulphonic acid has been prepared by Müller[269] by the action of sulphur trioxide on propyl alcohol.

Hessle[270] obtained synthetic tanning materials by treating mineral oils which contain unsaturated hydrocarbons with oleum (containing 20 to 30 per cent free sulphuric anhydride) at a relatively low temperature. The sulphonated products are said to consist principally of sulphones with relatively small proportions of sulphonic acids.[271]

The conversion of unsaturated aliphatic hydrocarbons containing 10 to 18 molecules or cracked petroleum fractions into wetting agents by the action of sulphuric acid at 0° C. in the presence of a diluent has been proposed. Olefins which have been sulphonated in this manner include tetradecene, octadecene, dodecene, a mixture consisting mainly of cetenes from the distillation of spermacetti, and olefins from the dehydration of oxidation products of naphthenes.[272] The sulphuric esters can be used together with soaps, Turkey-red oils, polynuclear aromatic sulphonic acids, glues, gelatine or mucilage, solvents, bleaching agents, or salts such as sodium chloride, bicarbonate, silicate, carbonate or sulphate. Decylene, and cetylene (hexadecylene) from the distillation of spermacetti, have likewise been sulphonated to give wetting agents by treatment in butyl alcohol solution at —5° C. with concentrated sulphuric acid.[273] The resulting product is washed with saturated sodium sulphate solution to remove the excess acid. The sulphation may be carried out also with chlorosulphonic acid, oleum or mixtures of sulphuric acid with acetic anhydride, acetyl or propionyl chloride, phosphorus chloride or pentoxide, boron trioxide or with sulphur trioxide dissolved in trichloroethylene, ethyl acetate, or ether.[274]

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[266] U. S. Patent 1,881,172, Oct. 4, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 575; *cf.* I. G. Farbenindustrie A.-G., French Patent 705,081, 1930; *Chem. Abs.*, 1931, **25**, 5259.

[267] I. G. Farbenindustrie A.-G., French Patent 715,585, 1931; *Chem. Abs.*, 1932, **26**, 2026.

[268] I. G. Farbenindustrie A.-G., French Patent 40,987, 1931; addition to French Patent 703,466, 1930; *Chem. Abs.*, 1933, **27**, 1524; *ibid.*, 1931, **25**, 4414.

[269] *Ber.*, 1873, 6, 1442.

[270] U. S. Patent 1,830,320, Nov. 3, 1931. *Cf.* Moeller, U. S. Patent 1,236,468, Aug. 14, 1917; *J.S.C.I.*, 1917, **36**, 1020; German Patent 262,333, 1912; *J.S.C.I.*, 1913, **32**, 878; both patents assigned to Gerb- und Farbstoffwerke H. Renner und Co.

[271] *Cf.* Condrea, *Rev. pétrol.*, 1911, 61; see Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, 1932, 416.

[272] I. G. Farbenindustrie A.-G., British Patent 343,872, 1929; *Brit. Chem. Abs.* **B**, 1931, 622; French Patent 693,814, 1930.

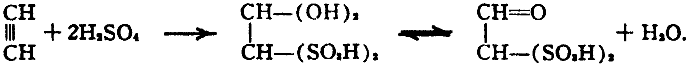
[273] H. T. Böhme A.-G., British Patent 360,602, 1930; *Brit. Chem. Abs.* **B**, 1932, 252.

Olefins resulting from the destructive oxidation of paraffin wax and naphthenic hydrocarbons have been sulphonated to give washing and emulsifying agents and especially textile reagents. Beller and Schuette [275] oxidized soft paraffin wax by blowing with air at 160° C. for 6 hours and removing with an alkaline wash the acid constituents which resulted from the oxidation. Unsaponifiable bodies were separated by centrifuging at about 20° C., thereby obtaining a liquid fraction consisting mainly of hydroxylated compounds. This liquid portion was heated at 180° to 220° C. with zinc chloride or concentrated sulphuric acid to bring about dehydration and formation of olefins. The olefin mixture (100 parts) was vigorously stirred at 15° C. with 80 parts of oleum containing 23 per cent of sulphur trioxide. The temperature was then raised to 25° to 30° C. and the reaction mixture stirred for about 5 hours until it was found to be soluble in water. In another case Russian gas oil was oxidized with air at about 160° C. in the presence of a small quantity of manganese naphthenate until the oil had a saponification value of 170. The product was distilled *in vacuo*. The saponifiable constituents were separated from the distillate by saponification with alkalies, and the unsaturated hydrocarbons recovered from the unsaponifiable fraction by distillation. 100 parts of the olefins thus obtained were converted into sulphonic acids by warming them with a mixture of 30 parts of acetic anhydride and 30 parts of sulphuric acid monohydrate at about 35° C. After the reaction mixture has become soluble in water, which is the case after from about 5 to 6 hours, the batch is poured onto ice, then neutralized. The sulphonic acids obtained cannot be saponified by boiling with aqueous mineral acid. Chlorosulphonic acid also has been used by Beller and Schuette to produce sulphonic acids from olefins of similar derivation.

The sodium salts of sulphonated carbazoles of olefins containing more than 2 carbon atoms are said to increase the wetting and emulsifying properties of aqueous solutions.[276]

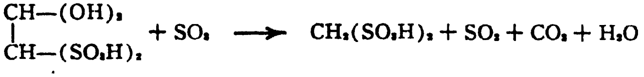
Products of the condensation of isethionic acid with aliphatic acids have been used in the washing and dyeing of wool.[277] Soaps can also be prepared by mixing these condensation products with stearin soaps and glycerol, for example, or with Marseilles soap.[277a]

Acetylene is absorbed by fuming sulphuric acid with evolution of much heat. The first stage of the reaction is:



$$\begin{array}{c}\mathrm{CH}\\ \|\!|\\ \mathrm{CH}\end{array} + 2H_2SO_4 \longrightarrow \begin{array}{l}\mathrm{CH{-}(OH)_2}\\ |\\ \mathrm{CH{-}(SO_3H)_2}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{CH{=}O}\\ |\\ \mathrm{CH{-}(SO_3H)_2}\end{array} + H_2O.$$

Oxidation by sulphur trioxide occurs and methane disulphonic acid [278] (methionic acid) is formed:



$$\begin{array}{l}\mathrm{CH{-}(OH)_2}\\ |\\ \mathrm{CH{-}(SO_3H)_2}\end{array} + SO_3 \longrightarrow CH_2(SO_3H)_2 + SO_2 + CO_2 + H_2O$$

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[274] I. G. Farbenindustrie A.-G., British Patent 358,583, 1930; *Brit. Chem. Abs.* B, 1932, 173.

[275] Beller and Schuette, U. S. Patent 1,914,321, June 13, 1933; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, 27, 4435.

[276] Michel and Buschmann, German Patent 552,606, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 5714.

[277] I. G. Farbenindustrie A.-G.; French Patent 712,121, 1931; *Chem. Abs.*, 1932, 26, 2067.

[277a] I. G. Farbenindustrie A.-G., French Patent 712,913, 1931; *Chem. Abs.*, 1932, 26, 1820.

[278] Muthmann, *Ber.*, 1898, 31, 1880; Schröter, *Ber.*, 1898, 31, 2190.

REACTIONS OF CHLOROSULPHONIC ACID WITH OLEFINS

With ethylene, chlorosulphonic acid forms ethylsulphuryl chloride (see Chapter 14), as has been shown by Müller[279] and Baumstark.[280] On prolonged treatment, however, with an excess of chlorosulphonic acid, ethionyl chloride results.[281] If this latter product is warmed, hydrogen chloride is evolved and an oil remains which slowly congeals. When treated with water, this oil yields the anhydride of isethionic acid, $C_2H_4SO_3$, and the anhydride ($C_2H_6SO_5$) of an acid $C_2H_8SO_6$, as well as the acids themselves.[282] The action of chlorosulphonic acid on the higher olefins has been but cursorily investigated. However, Marcusson[283] observed that petroleum asphalts reacted violently with chlorosulphonic acid with the evolution of large quantities of hydrogen chloride. In a chloroform solution the reaction proceeds quietly and addition compounds which contain chlorine and sulphur are formed.

Condensation of olefins with chlorosulphonic acid in the presence of esters or ethers of low molecular weight at temperatures above 100° C. yields true sulphonic acids stable to boiling hydrochloric acid.[284]

SULPHONATION OF AROMATIC HYDROCARBONS

Although the action of sulphonating agents on aromatic hydrocarbons is outside the scope of this book, nevertheless mention should be made of the few instances in which derivatives of aromatic hydrocarbons have been obtained from petroleum. The formation of these aromatic hydrocarbons may be the result of dehydrogenation of naphthenes,[285] as discussed in the section on the sulphonation of cycloparaffins.

By treating various light fractions of a Bustenari petroleum with fuming sulphuric acid (containing 12 per cent sulphur trioxide) at 80° C., Edeleanu and Gané[286] obtained tarry and resinous materials insoluble in water. On distillation with steam the substances yielded about 4.6 per cent of xylene, mesitylene, pseudocumene and hydrocarbons of unknown structure. Hausmann[287] obtained very little phenol on fusing sulphonic acids from a Galician petroleum distillate with sodium or potassium hydroxide.

According to Starke,[288] the naphthenes of a petroleum fraction boiling between 130° to 260° C. give aromatic sulphonic acids when treated with 96 per cent sulphuric acid at 70° to 130° C. Benzene can be recovered from the sludge by distillation with superheated steam.

Popa and Velculescu[289] studied the direct sulphonation of petroleum hydrocarbons in both vapor and liquid phase with 98.8 per cent sulphuric acid. After separation of the sulphonated mixture from the unreacted hydrocarbons, it was subjected to distillation with superheated steam, the mixture being kept at 180°

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[279] *Ber.*, 1873, 6, 227. See also Traube and Justh, *Brennstoff-Chem.*, 1923, 4, 150; *Chem. Abs.*, 1923, 17, 3858.

[280] *Z. für Chemie*, 1867, 566.

[281] Claesson, *J. prt. Chem.*, 1879, (2) 19, 234; *Chem. Soc. Abs.*, 1879, 36, 1033.

[282] See Baumstark, *loc. cit.*, and Claesson, *loc. cit.*

[283] *Chem.-Ztg.*, 1915, 39, 581; *Petroleum Z.*, 1916, 12, 1149.

[284] Haussmann, German Patent 550,243, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 4067; British Patent 364,669, 1930; *Brit. Chem. Abs.* B, 1932, 495.

[285] See also Tilitschejev and Dumiskaja, *Neft. Khoz.*, 1927, 13, 647; *Brit. Chem. Abs.* B, 1928, 630.

[286] *Moniteur Roum.*, 1908, 493; *Oesterr. Chem. Tech. Ztg.*, 1908, 26, 156; *Chem. Abs.*, 1909, 3, 1079; see Gurwitsch-Moore, "Scientific Principles of Petroleum Technology, D. Van Nostrand Co., New York, 1932, 392.

[287] *Petroleum Z.*, 1910, 6, 2301; *Chem. Abs.*, 1912, 6, 681; see also von Pilat and Starkel, *Petroleum Z.*, 1912, 6, 2177; *Chem. Abs.*, 1911, 5, 3729.

[288] U. S. Patent 913,780, Mar. 2, 1909; *J.S.C.I.*, 1909, 28, 360.

[289] *Bul. chim. soc. romane chim.*, 1930, 33, 3; *Chem. Abs.*, 1932, 26, 5405.

to 190° C. The aromatic sulphonic acids were thus decomposed and the regenerated hydrocarbons passed over with the steam. Sulphonation in vapor phase required such a high temperature that both naphthenic and paraffin hydrocarbons also reacted with considerable evolution of sulphur dioxide. In the liquid phase, sulphonation was easily conducted at 60° C. The aromatic hydrocarbons recovered contained about 0.5 per cent of other hydrocarbons.

SULPHONATION OF SULPHUR-CONTAINING SHALE OILS

Since the sixteenth century the peasants of the Tyrol have been known to distil the local shale, rich in fossil fish, to obtain a tarry oil which they employed to cure sores and wounds on live stock.[290] In 1890 the name "ichthyol" was given to this oil by Schröter of Hamburg.[291] The oil when treated with sulphuric acid yields ichthyolsulphonic acid which contains about 10 to 15 per cent sulphur, and forms salts with alkali metals or ammonia. The ammonium salt is generally known in commerce as ichthyol and is used for its therapeutic effects in skin diseases. Various other preparations, which include the odorless desichthyol obtained by distilling ichthyol with steam or by treating it with hydrogen peroxide, and the blackish-brown ichthyoform prepared from ichthyolsulphonic acid and formaldehyde are also used for similar purposes.[292] Alderson[293] has given a summary of the deposits and extent of these ichthyol shales and the volume of the industry. Some fractions of the oils have sharp odors and are said to kill flies instantly.[294]

The composition of the ichthyol oil has not been completely determined. Scheibler[295] concluded that the oil contains higher homologues of thiophene (in some cases 50 per cent of the oil) together with hydrocarbons of the benzene series and small proportions of compounds richer in hydrogen. According to Baumann and Schotten,[296] ichthyolsulphonic acid has the formula $C_{28}H_{26}S(SO_3H)_2$.

The sulphonation of shale oil distillates to produce ichthyolsulphonic acids is carried out in a manner similar to that of mineral oil fractions. The purification of the products can be accomplished in a number of ways, the earliest probably being that of precipitating the sulphonic acid from an aqueous solution with salt or with hydrochloric acid.[297]

Helmers[298] recovered the ichthyolsulphonic acids from the mixture by neutralizing them with an alkali and separating with solvents such as alcohol, benzene, and chloroform. The ichthyolsulphonates of the alkaline earths or heavy metals are rendered tasteless by extraction with alcohol[299] or by heating[300] up to about 140° C.

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[290] Zwingaur (German Patent 216,906, 1907; *Chem. Abs.*, 1910, **4**, 1224) described the distillation of ichthyol shale with steam in vacuum to obtain oils with higher specific gravities and viscosities.

[291] Alderson, *Quart. Colorado School of Mines*, 1923, **18** (1), Suppl. B; see Helmers, *Pharm. Centr.*, 1897, **38**, 716; *Chem. Zentr.*, 1897, **2**, 1076.

[292] Molinari, "Treatise on General Industrial Chemistry," translated by Pope, P. Blakiston's Sons and Co., Philadelphia, **1913**, 84.

[293] *Loc. cit.*

[294] Belani, *Petroleum Z.*, 1925, **21**, 1439; *Chem. Abs.*, 1926, **10**, 477.

[295] *Ber.*, 1915, **48**, 1815; *Chem. Abs.*, 1916, **10**, 340.

[296] See Thorpe, "Dictionary of Applied Chemistry," Longmans, Green and Co., New York, **1912**, 3, 92.

[297] Schröter, U. S. Patent 318,662, May 26, 1886; U. S. Patent 513,204, Jan. 23, 1894; British Patent 10,523, 1884; all patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co. Jacobsen, U. S. Patent 495,343, 1893; German Patent 38,416, 1886; *Chem. Zentr.*, 1887, 395; German Patent 54,501, 1889; *Chem. Zentr.*, 1891, **1**, 688; German Patent 78,835, 1893; *Chem. Ztg.*, 1895, **19**, 310; British Patent 10,695, 1886. Fr. Rosé and Co., German Patent 101,807, 1897; *Chem. Ztg.*, 1899, **23**, 253. Helmers, German Patent 76,128, 1893; assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.; *Chem. Zentr.*, 1894, **2**, 911; Soc. Anon. de la Thyoléine, German Patent 169,356, 1903; *Chem. Zentr.*, 1906, **1**, 1583; French Patent 353,708, 1905; *Chem. Abs.*, 1907, **1**, 382.

[298] U. S. Patent 525,784, Sept. 11, 1894; British Patent 6,044, 1893; *J.S.C.I.*, 1894, **13**, 508; German Patent 82,075, 1893; *Chem. Zentr.*, 1895, **2**, 744; all patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.

Oxidation of the ichthyolsulphonic acids with agents such as hydrogen peroxide has also been used to render them odorless and tasteless.[301]

The separation of ichthyolsulphonic acids into fractions of various sulphur contents has been effected with aniline, piperazine, or dimethylphenylpyrazolone.[302] As a result of the difference in solubility in water of the double compounds of these sulphonic acids, fractions rich and poor in sulphur can be obtained. The sulphonic acids can be recovered by decomposing the compounds with mineral acids.

Purification of ichthyolsulphonic acids has also been effected by treatment with steam under reduced pressure.[303] For the removal of inorganic salts, dialysis has been proposed.[304]

As a means of purification, double complex compounds of the ichthyolsulphonic acids with albumen[305] and formaldehyde[306] have also been formed. These precipitate from solution and can be used as such in various pharmaceutical preparations, the product with formaldehyde being called ichthyoform, as mentioned previously.

Besides the therapeutic uses for ichthyol-sulphonic acids, they have been suggested by Helmers[307] for bringing phenols and hydrocarbons into solution.

Schaeffer and Faber[308] sulphonated sulphur-containing shale oil distillates with chlorosulphonic acid to obtain disinfectants. The resulting soluble brown mass was called sulphothalassolic acid and its ammonium salt was termed thalassol.

The sulphonic acids prepared by treating the unsaturated hydrocarbons present in middle and higher petroleum fractions, mineral waxes or rosin oils with sulphuric acid have been called tumenolsulphonic acids.[309] These have also been recommended for pharmaceutic purposes. Mineral oil, for example,[310] was heated with fuming sulphuric acid (10 per cent sulphur trioxide) at 80° C. The reaction mixture was dissolved in water and the sulphonic acids and sulphones were precipitated by the addition of salt solution. Sulphonic acid salts were thus formed and the sulphones were removed from them in this precipitate by extraction with ether, naphtha, or similar solvents. The tumenolsulphones were said[311] to have the formula $(C_{41}H_{67}O)_2SO_2$ and the tumenolsulphonic acids, $C_{41}H_{62}O_2SO_3$. These tumenolsulphonic acids have the property of precipitating glue and gelatin from slightly acid solutions with the formation of an elastic rubber-like precipitate which can be drawn into threads.[312]

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[299] Helmers, U. S. Patent 624,027, May 2, 1899; German Patent 99,124, 1897; *Chem. Zentr.*, 1898, **2**, 1192; German Patent 107,233, 1899; *Chem. Zentr.*, 1900, 1, 886; German Patent 112,630, 1899; *Chem. Zentr.*, 1900, **2**, 462; German Patent 114,393, 1899; *Chem. Zentr.*, 1900, **2**, 996; British Patent 5,004, 1898; *J.S.C.I.*, 1899, **18**, 398; all patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co. See also Helmers, *Pharm. Z.*, 1899, **45**, 859; *Pharm. J.*, 1899, **62**, 181; *J.S.C.I.*, 1899, **18**, 397.

[300] Helmers, U. S. Patent 624,028, May 2, 1899; British Patent 5,004, 1898; *J.S.C.I.*, 1899, **18**, 398; both patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.

[301] Helmers, German Patent 99,765, 1897; *Chem. Zentr.*, 1899, 1, 464; German Patents 114,394 and 114,395, 1899; *Chem. Zentr.*, 1900, **2**, 996; German Patents 120,014 and 120,015, 1899; *Chem. Zentr.*, 1901, **1**, 1073; German Patent 127,505, 1901; *Chem. Zentr.*, 1902, 1, 235; British Patent 10,875, 1898; *J.S.C.I.*, 1899, **18**, 606; British Patent 14,389, 1899; *J.S.C.I.*, 1900, **19**, 653; British Patent 17,346, 1899; *J.S.C.I.*, 1900, **19**, 923; all patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.

[302] Helmers, U. S. Patents 671,135, Apr. 2, 1901; 709,321, Sept. 16, 1902; *J.S.C.I.*, 1902, **21**, 1296; British Patent 6,795, 1901; *J.S.C.I.*, 1900, **19**, 364; all patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.

[303] Knoll and Co., German Patent 100,707, 1897; *Chem. Zentr.*, 1899, 1, 766; German Patent 118,452, 1899; *Chem. Zentr.*, 1901, **1**, 603; German Patent 124,144, 1899.

[304] G. Hell and Co., German Patent 161,663, 1900; *J.S.C.I.*, 1905, **24**, 1008.

[305] Helmers, U. S. Patent 649,305, May 8, 1900; British Patent 14,388, 1899; *J.S.C.I.*, 1900, **19**, 688; both patents assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.

[306] Helmers, British Patent 9,157, 1899; assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co., *J.S.C.I.*, 1900, **19**, 337.

[307] Helmers, German Patent 76,133, 1893; *Chem. Zentr.*, 1894, **2**, 911; German Patent 80,260, 1893; *Chem. Zentr.*, 1895, **1**, 1096; both assigned to Ichthyol Gesellschaft Cordes, Hermanni and Co.

[308] British Patent 166,727, 1920; *Chem. Abs.*, 1922, **16**, 792.

[309] Gewerkschaft Messel, German Patent 56,401, 1890; *Chem. Ztg.*, 1891, **15**, 772; *Chem. Zentr.*, 1891, **2**, 336. German Patent 65,850, 1891; *Chem. Zentr.*, 1893, **1**, 912. British Patent 19,502, 1890; *J.S.C.I.*, 1892, 11, 22.

[310] *Cf.* Gewerkschaft Messel, German Patent 65,850, 1891; *Chem. Zentr.*, 1893, 1, 912.

Another method of making hydrocarbons with high sulphur contents and of therapeutic value is that described by Bengough.[313] Unsaturated hydrocarbons formed on the distillation of sulphonated mineral oils in the presence of lime were treated with 10 to 40 per cent sulphur chloride. This yielded a thick brown oil which contained both chlorine and sulphur. When this oil was boiled with a 10 per cent sodium hydroxide solution, the chlorine was removed and a product containing about 30 per cent sulphur was obtained.

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[311] Gewerkschaft Messel, German Patent 56,401, 1890. See also Dieckhoff, *Dinglers Polytech. J.*, 1892, 287, 41; *Chem. Zentr.*, 1893, 1, 375.

[312] Gewerkschaft Messel, British Patent 19,502, 1890; *J.S.C.I.*, 1892, 11, 22.

[313] German Patent 138,345, 1901; Austrian Patent 6,246, 1900; *Chem. Zentr.*, 1903, 1, 305; British Patent 8,596, 1903; *J.S.C.I.*, 1904, 23, 383.

Chapter 47

Chemical Action of Nitric Acid, Nitrosyl Chloride and Various Other Reagents on Saturated Hydrocarbons

Saturated paraffin hydrocarbons are regarded as highly resistant to chemical reagents, and this characteristic has received undue and unjustified emphasis. While the gaseous members of the series are extremely stable and chemically inert, this is by no means true of all paraffins. Some of the branched chain paraffins exhibit a surprising degree of chemical activity, and a number of reactions formerly considered characteristic of aromatic hydrocarbons only are now known to occur with both the paraffins and cycloparaffins—though rarely, be it admitted, with a facility equalling that of unsaturated ring compounds.

Of the cycloparaffins, the cyclopropanes and cyclobutanes are considerably more reactive, as a class, than the cyclopentanes and cyclohexanes. The action of chemical reagents often ruptures three- and four-carbon ring systems with production of straight chain derivatives. Since only the five- and six-carbon ring compounds have been found in any quantities in the lower-boiling fractions of petroleum, these two series will be considered representative of cycloparaffins in the following account. In general, the chemical reactivities of the cyclopentanes and cyclohexanes are similar to those of the paraffins. However, some of their homologues are far from indifferent to various reagents.

The saturated hydrocarbons of the paraffin and cycloparaffin series are sharply differentiated from the unsaturated hydrocarbons (olefins, diolefins, or acetylenes) in that the former yield substitution compounds exclusively with various chemical reagents, while the latter can form direct addition compounds (though both addition and substitution reactions may take place simultaneously with some unsaturated hydrocarbons). This fundamental difference between saturated and unsaturated hydrocarbons is exemplified by the combination of chlorine with methane, representing the saturated hydrocarbons, and with ethylene typical of the unsaturated type. The reactions taking place are illustrated by the following equations:

(1) *Substitution Reactions*

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

(2) *Addition Reaction*

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

Although the paraffins possess high chemical stability at the temperatures ordinarily employed in the more usual chemical reactions, at higher temperatures their thermodynamic stability is materially reduced. With the exception of the first few (lower) members of the series, the paraffins pyrolyze at elevated temperatures much more readily than other hydrocarbons, and, in this respect, are markedly less stable than the olefin and aromatic hydrocarbons. Saturated hydrocarbons possess no power of polymerization, a property belonging exclusively to unsaturated substances.

The paraffins of low molecular weight are least reactive toward the usual chemical reagents, but the resistance of the homologues of increasing molecular weight to oxidation and other chemical changes, so characteristic of the lower members, is reduced. The branched chain members containing a tertiary carbon atom (i.e., a carbon atom attached directly to three other carbon atoms) exhibit a greater tendency to react chemically, as with nitric or chlorosulphonic acid, than do the straight chain members, but the quaternary paraffins (i.e., paraffins containing a carbon atom linked to four other carbon atoms) are very stable.

In the following account a review is presented of the reactions of the paraffins and cycloparaffins (the latter class being restricted in this discussion to the cyclopentanes and cyclohexanes) with various chemical reagents. Attention is specially directed, as far as possible, to those reactions which appear capable of use in the conversion of these saturated hydrocarbons into chemical products.

NITRATION OF PARAFFIN HYDROCARBONS

Unlike the aromatic and the unsaturated hydrocarbons, the paraffins, in general, are not attacked at ordinary temperatures by concentrated or fuming nitric acid or by mixtures of nitric and sulphuric acids. Francis and Young[1] found the order of reactivity of hydrocarbons with fuming nitric acid to be as follows: (1) aromatic compounds[2] and methyl derivatives of the cycloparaffin hydrocarbons, which react at ordinary temperatures; (2) the tertiary paraffins (characterized by the presence of a branched chain and the $\equiv$CH grouping), which are attacked when heated moderately on a water-bath; (3) the cycloparaffin compounds; and (4) the normal (i.e., straight chain) paraffins. Both of the latter types are slowly attacked on heating on a water-bath. Quaternary hydrocarbons, however, were found by Markownikow[3] to react as slowly as normal paraffins.

The relative yields of oxidation and nitration products obtained in the treatment of hydrocarbons with nitric acid (or with mixtures of nitric and sulphuric acids[4]) depend largely on the following factors: (1) the temperature, (2) the concentration of the nitric acid employed, (3) the pressure,[5] i.e., whether the experiment is carried out in sealed tubes or in open vessels, (4) the duration of heating,[6] and (5) the structure of the particular hydrocarbon under treatment.

It was shown by Konowalow[7] that a very effective method of preparing nitrated products from paraffins consists in heating the paraffin with relatively dilute nitric acid (sp. gr. 1.075) at temperatures over 100° C. Under these conditions, quantities of mono- and di-nitrated products may be obtained from a wide variety of paraffins. Nitro-compounds can also be produced[8] by the action of more concentrated acid at lower temperatures (specific gravity 1.535 at above 0° C., for example) but under these conditions oxidation reactions occur easily. Worstall [9] secured a 60 per cent yield of nitrated products (containing both mono- and di-nitro-compounds) by boiling n-hexane for several days with concentrated nitric acid (specific gravity 1.52 or 1.42), either alone or with concentrated sulphuric acid. An investigation of the influence of acid concentration by Poni and Costachescu [10] revealed that, while isopentane could be nitrated with difficulty by acid of a specific gravity 1.075 to 1.14 at temperatures below 140° C., higher concentrations (specific gravity 1.38 to 1.42) attacked this hydrocarbon readily at 60° C., yielding both nitrated and oxidized products. The best yields of nitro compounds (mono-, di-, and tri-nitro-compounds being produced) were obtained at 60° C. with acid of specific gravity 1.42, using 1.5 moles of acid to 1 mole of hydrocarbon. The action of fuming nitric acid on various isoparaffins at their boiling points was investigated by Francis and Young,[1] who noted the formation of oxidation and nitration products from isohexane, isoheptane, and isooctane. Solid trinitro-compounds were obtained from isohexane and isoheptane.

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[1] *J.C.S.*, 1898, **73**, 928.

[2] See also Konowalow and Gurewitsch, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 537; *Chem. Soc. Abs.*, 1905, **88** (1), 763.

[3] *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 530; *Chem. Zentr.*, 1899, **2**, 473. Also *Ber.*, 1899, **32**, 1445; *Chem. Soc. Abs.*, 1899, **76** (1), 554.

[4] The behavior of concentrated nitric acid and mixtures of nitric acid and sulphuric acid is discussed by Markownikow (*Ber.*, 1899, **32**, 1441; *Chem. Soc. Abs.*, 1899, **76** (1), 553).

[5] See Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 57; *Chem. Zentr.*, 1899, **1**, 1063; *Chem. Soc. Abs.*, 1899, **76** (1), 844.

[6] Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 109, 124; *Chem. Soc. Abs.*, 1907, **92** (1), 1.

[7] *J. Russ. Phys.-Chem. Soc.*, 1893, **25**, 472; *Chem. Soc. Abs.*, 1894, **66** (1), 265; *Ber.*, 1895, **28**, 1852; *Chem. Soc. Abs.*, 1895, **68** (1), 633. See also *Ber.*, 1896, **29**, 2199; *Chem. Soc. Abs.*, 1896, **70** (1), 673.

[8] Markownikow, *Ber.*, 1899, **32**, 1441; *J. prt. Chem.*, 1899, **59** (2), 556; *Chem. Zentr.*, 1899, **2**, 179.

Of the paraffin hydrocarbons, the tertiary paraffins, containing the characteristic grouping R_3CH, appear to be most easily nitrated, yielding the tertiary nitro-compounds very readily. In the nitration of the paraffin hydrocarbons, the entering nitro-group has the greatest tendency to become attached to a tertiary carbon atom. When no tertiary carbon atom is present the nitro-group tends to attach itself to a secondary rather than primary carbon atom.[11] In general, quaternary paraffins of the type R_4C are nitrated only with difficulty and may often be separated from the other types of paraffins by this characteristic.[12] The orientation of the entering nitro-group appears to depend somewhat upon the strength of nitric acid used.

Direct nitration of paraffins containing less than five carbon atoms in the molecule apparently has not been effected. However, in the purification of a fraction of Caucasian petroleum boiling between 40° and 50° C. by treatment with nitric acid of specific gravity 1.52, Beilstein and Kurbatow [13] recovered a compound, $C_4H_8N_2O_4$. This compound crystallized in glistening needles, melting at 96° C., soluble in alcohol, ether, carbon disulphide and light petroleum, and shown to be identical with a compound prepared by Haitinger [14] from isobutylene and concentrated nitric acid. The constitution of the dinitro-compound is somewhat uncertain; it does not correspond to any of the isomeric dinitrobutanes. Since the 40° to 50° C. fraction is practically free from butanes or other lower hydrocarbons, this nitro-compound must have been formed from products of the decomposition of hydrocarbons of higher molecular weight arising through the action of nitric acid.

Isopentane was found by Francis and Young [15] to yield what was probably a trinitro-derivative by boiling with fuming nitric acid under a reflux apparatus for a prolonged period. Later Poni and Costachescu [10] thoroughly investigated the nitration of this hydrocarbon. With nitric acid of specific gravity 1.075 to

[9] *Amer. Chem. J.*, 1898, **20**, 202; *Chem. Soc. Abs.*, 1898, **74** (1), 346.

[10] *Ann. Sci. Univ. Jassy*, 1903, **2**, 119; *Chem. Soc. Abs.*, 1903, **84** (1), 596; see also Poni, *Ann. Sci. Univ. Jassy*, 1902, **1**, 53; *Chem. Soc. Abs.*, 1902, **83** (1), 581.

[11] Konowalow, *Compt. rend.*, 1892, **114**, 26; *Chem. Soc. Abs.*, 1892, **62** (1), 575; (See correction in *Ber.*, 1892, **25**, 1244). However, Worstall, (*Amer. Chem. J.*. 1898, **20**, 202; 1899, **21**, 210, 218) describes the conversion of n-hexane and n-octane into *primary* nitro-compounds by nitration with nitric acid of sp. gr. 1.52 or 1.42 in an open vessel at the boiling point of the hydrocarbon.

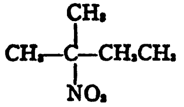
[12] Markownikow, *Ber.*, 1899, **32**, 1441; *Chem. Soc. Abs.*, 1899, **76** (1), 553.

[13] *Ber.*, 1881, **14**, 1620; *Chem. Soc. Abs.*, 1881, **40**, 1020.

[14] *Monatsh.*, 1881, **2**, 287.

[15] *J.C.S.*, 1898, **73**, 928.

1.14 at temperatures somewhat below 140° C. in sealed tubes, isopentane was slowly nitrated to yield the tertiary nitro-compound, *2-nitro-2-methylbutane,*



$$CH_3-\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_3$$

Stronger acid (specific gravity 1.42) at 60° C. yielded products consisting of the above mononitro-compound, *2,3-dinitro-2-methylbutane* (boiling point 105° to 110° C. at 44 mm., and d_0^0 1.1572), *2,3,4-trinitro-2-methylbutane* (a crystalline solid melting at 179° to 184° C.) together with some 1-hydroxyisobutyric acid, oxalic acid and carbon dioxide.

The nitration of *n-hexane* has been the subject of a number of studies. Konowalow[16] reported that though nitric acid of specific gravity 1.155 nitrates n-hexane at 115° to 120° C. in a sealed tube, the yield of the mononitro-compound is low. Better results are procured by using acid of specific gravity 1.075 at 140° C. Under the latter conditions a 60 per cent yield of nitrohexane (boiling point 176° C. at 758 mm. and d_0^0 0.9509) is obtained. This was proved to be the secondary nitro-compound, *2-nitrohexane,* since on reduction with zinc and acetic acid it yielded methyl butyl ketone and β-hexylamine. On the other hand, Worstall[17] found that if n-hexane is boiled for several days in an open vessel with nitric acid of a specific gravity 1.52 to 1.42, either alone or with sulphuric acid, a 60 per cent yield of nitrated products is obtained. These consisted of a primary nitrohexane (*1-nitrohexane*), a light yellow oil (boiling point 180°-183° C., which gave a nitrolic acid on treatment with nitrous acid), together with a *dinitrohexane* (probably also primary). The latter compound is sparingly soluble in aqueous alkalies, though readily so in alcoholic alkalies. It could not be distilled without decomposition. Reduction of this mononitrohexane by Worstall gave a primary amine.

From *isohexane,* Francis and Young obtained a crystalline trinitro-derivative (melting at 85.5°-86.0° C.) by refluxing that hydrocarbon with fuming nitric acid for 6 days. Oxidation products were also produced. A number of crystalline nitration products, apparently derivatives of isohexane, were prepared by Zaloziecki and Frasch[18] by nitration of fractions of Galician petroleum (boiling range, 45° to 65° C.) using a mixture of 1 part of nitric acid (specific gravity 1.404) and 3 parts of concentrated sulphuric acid. The products were fractionally crystallized from alcohol yielding (1) yellow needles, melting point 89.5° C., (2) a substance of melting point 67° C., and (3) two other substances crystallizing in needles and melting at 65° C. and 61° C., respectively. An extensive investigation of the nitration of an isohexane (3-methylpentane) is that of Poni and Costachescu,[19] who used a fraction, boiling at 61.5°-62.5° C., of a Rumanian crude. This fraction was nitrated with nitric acid of specific gravity 1.4 in sealed tubes at 60° C., and the nitrated products were dried and fractionated under a pressure of 35 mm. More than half of the product distilled at 75°-76° C. and this appeared to be the expected tertiary mononitro-derivative, i.e., *3-nitro-3-methylpentane,* boiling point 168°-170° C. at 750 mm., and d_0^0 0.9681. The fraction of highest boiling point (150° to 158° C.) consisted of a dinitro-compound, but was obtained only in a relatively small amount. A quantity of unattacked hydrocarbon was identified as *2-methylpentane.*

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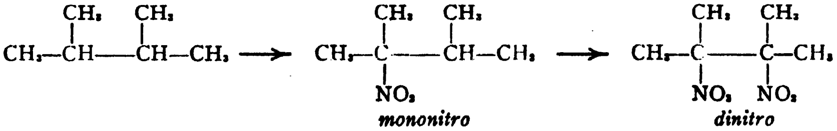
[16] *J. Russ. Phys.-Chem. Soc.,* 1894, **25**, 472; *Chem. Soc. Abs.,* 1894, **66** (1), 265.
[17] *Amer. Chem. J.,* 1898, **20**, 202; *Chem. Soc. Abs.,* 1898, **74** (1), 346.
[18] *Ber.,* 1902, **35**, 386; *cf.* Markownikow, *Ber.,* 1902, **35**, 1584.
[19] *Ann. Sci. Univ. Jassy,* 1904, **3**, 95; *Chem. Soc. Abs.,* 1905, **88** (1), 109.

Poni and Costachescu also examined the products of the action of fuming nitric acid (sp. gr. 1.525) on this Rumanian petroleum fraction. Two crystalline trinitro-compounds were identified, one of which proved to be *2,3,3-trinitro-2-methylpentane;* and the other, forming crystals of melting point 85° C., appeared to be *2,2,3-trinitro-3-methylpentane.* These were identical with the trinitro-derivatives isolated by Francis and Young.

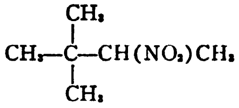
Like most of the di-tertiary paraffins, *diisopropyl* reacts readily with nitric acid at 20° C. It can be nitrated to yield a mononitro-compound, proved by Konowalow [20] to be the tertiary compound, *2-nitro-2,3-dimethylbutane,* a liquid of boiling point 168°-169° C. at 750 mm., and d_0^0 0.9716, together with a di-tertiary nitro-compound, *2,3-dinitro-2,3-dimethylbutane,* melting point 208° C. Konowalow [21] obtained these compounds not only from synthetic diisopropyl but also from fractions, boiling at 55° to 60° C., of American and Baku petroleums. The nitration of diisopropyl accordingly proceeds as follows:



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3 \longrightarrow CH_3{-}\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3 \longrightarrow CH_3{-}\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3}$$

mononitro *dinitro*

The typical quaternary paraffin, *trimethylethylmethane*, can be nitrated, though with difficulty, to yield a crystalline mono-nitroderivative of melting point 40° and boiling point 167.5°-167.8° C. at 748 mm. This substance has been proved by Markownikow [22] to possess the structure



$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH(NO_2)CH_3}$$

since, on reduction with alkaline stannous chloride, it yields the oxime of pinacoline, while reduction with tin and hydrochloric acid gives the corresponding *β*-amine, a liquid of boiling point 101.5°-102.5° C. *2,2-Dimethylpentane* (trimethylpropylmethane) has also [23] been nitrated to give *2,2-dimethyl-3-nitropentane,* of d_0^0 0.9520, boiling point 89°-90° C. under 40 mm. pressure. It appears to be a general rule with hydrocarbons of this type that nitration takes place in such a way that the nitro-group becomes attached to the carbon atom next to the $(CH_3)_3C$— group.

Beilstein and Kurbatow [24] obtained a nitro-compound by treating a crude American petroleum fraction boiling between 115° and 120° C. with nitric acid. The nitrated fraction boiling between 193° and 197° C. was found to correspond to the formula $C_7H_{15}NO_2$. Konowalow [25] nitrated *n-heptane* by heating it in a sealed tube with dilute nitric acid (of sp. gr. 1.075) at 125° to 130° C. A secondary nitro-derivative, *2-nitroheptane,* a liquid of boiling point 194°-196° C. and d_0^{20} 0.9306, resulted. This secondary nitroheptane appears to be identical with the compound of Beilstein and Kurbatow.

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[20] *Ber.,* 1895, 28, 1852; *Chem. Soc. Abs.,* 1895, 68 (1), 633; *J. Russ. Phys.-Chem. Soc.,* 1893, 25, 498.

[21] *J. Russ. Phys.-Chem. Soc.,* 1905, 37, 1119; *Chem. Zentr.,* 1906, 1, 737.

[22] *Ber.,* 1899, 32, 1445; *Chem. Soc. Abs.,* 1899, 76, (1), 554.

[23] Markownikow, *Ber.,* 1900, 33, 1905; *Chem. Soc. Abs.,* 1900, 78 (1), 469.

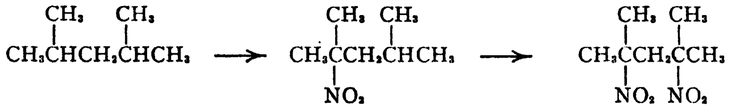
[24] *Ber.,* 1880, 13, 2028; *Chem. Soc. Abs.,* 1881, 40, 159.

[25] *J. Russ. Phys.-Chem. Soc.,* 1893, 25, 472; *Chem. Soc. Abs.,* 1894, 66 (1), 265.

According to Worstall,[26] normal heptane is much more readily nitrated than n-hexane by boiling the hydrocarbon with nitric acid of specific gravity 1.42 to 1.52. The product was said to consist of a primary nitroheptane (boiling at 193° to 196° C.), giving a nitrolic acid with nitrous acid, and readily reducible to a primary amine. A primary dinitroheptane, $CH_3(CH_2)_5CH(NO_2)_2$, was also obtained under these conditions.

A study of the reactions of nitrogen pentoxide with benzene, bromobenzene, toluene, phenol, benzoic acid, m-dinitrobenzene, pyridine, triethylamine and other compounds by Haines and Adkins[27] revealed that heptane was rapidly and quantitatively nitrated at 0° C. The products of the reaction decomposed on distillation at atmospheric pressure but a small amount of unidentified material which boiled at 130° to 180° C. at 25 mm. was obtained.

Of the branched chain heptanes, an *isoheptane* from petroleum was found by Francis and Young[28] to undergo nitration when refluxed with fuming nitric acid for two days. A crystalline trinitro-compound, of melting point 194° C., was isolated from the reaction mixture. Nitration of *2,4-dimethylpentane* by dilute nitric acid (d. 1.11) in sealed tubes leads to the formation of the tertiary mono- and di-nitro-derivatives.[29] The course of the nitration of 2,4-dimethylpentane is, therefore, as follows:



$$CH_3\overset{CH_3}{C}HCH_2\overset{CH_3}{C}HCH_3 \longrightarrow CH_3\underset{NO_2}{\overset{CH_3}{C}}CH_2\overset{CH_3}{C}HCH_3 \longrightarrow CH_3\underset{NO_2}{\overset{CH_3}{C}}CH_2\underset{NO_2}{\overset{CH_3}{C}}CH_3$$

2-nitro-2,4-dimethylpentane, b.p. 181°-182° C./742 mm. *2,4-dinitro-2,4-dimethylpentane,* m.p. 81°-82° C.

Nitration of *triethylmethane* with nitric acid of specific gravity 1.075 at 120° C. yields 57 per cent of a tertiary nitro-compound and 43 per cent of a mixture of primary and secondary nitro-compounds.[30]

The nitration of *n-octane* has been the subject of a number of studies. Konowalow[31] nitrated this hydrocarbon by heating it in a sealed tube at 130° C. with dilute nitric acid of specific gravity 1.075 and obtained a fair yield of the secondary nitro-compound, *2-nitrooctane,* a liquid of boiling point 210°-212° C., and d_0^{20} 0.9201. On the other hand, Worstall[32] reported the formation of primary mono- and di-nitrooctanes by boiling the hydrocarbon with nitric acid (specific gravity 1.42) and sulphuric acid. The use of fuming nitric acid (specific gravity 1.52) resulted in extensive oxidation of the hydrocarbon. The *primary mononitrooctane* was described by Worstall as a liquid boiling at 205° to 210° C., giving the nitrolic acid test and readily reducible to a primary amine.

Francis and Young[33] noted the formation of a liquid nitro-compound on refluxing an *isooctane* fraction from petroleum with fuming nitric acid. Of the branched chain octanes, diisobutyl (*2,5-dimethylhexane*) is readily nitrated at 105° to 110° C. by nitric acid (d. 1.075) to yield[34] a mixture of nitro-compounds consisting mainly of the tertiary mononitro-compound, *2-nitro-2,5-dimethylhexane,* a yellowish liquid of boiling point 200°-202° C. and d_0^0 0.9396. When this nitro-compound is further heated with dilute nitric acid at 120° to 125° C., the tertiary dinitro-compound, *2,5-dinitro-2,5-dimethylhexane*, a crystalline solid of melting point 124°-125° C., is produced. The nitration of this hydrocarbon can be represented thus:

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[26] *Amer. Chem. J.*, 1898, **20**, 202; *Chem. Soc. Abs.*, 1898, **74** (1), 346.

[27] *J.A.C.S.*, 1925, **47**, 1419; see Chapter 25 also.

[28] *J.C.S.*, 1898, **73**, 928; *Chem. Soc. Abs.*, 1908, **94** (1), 241.

[29] Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 1119; *Chem. Zentr.*, 1906, **1**, 737. See also Chonin, *ibid.*, 1909, **41**, 327; *Chem. Zentr.*, 1909, **2**, 587; *Chem. Soc. Abs.*, 1909, **96** (1), 450.

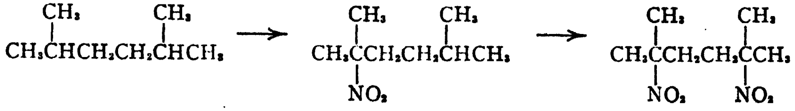
[30] Konowalow and Kotsina, *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 1027; *Chem. Soc. Abs.*, 1900, **78** (1), 324.

[31] *J. Russ. Phys.-Chem. Soc.*, 1894, **25**, 472; *Chem. Soc. Abs.*, 1894, **66** (1), 265.

[32] *Amer. Chem. J.*, 1898, **20**, 202; *Chem. Soc. Abs.*, 1898, **74** (1), 346.

[33] *J.C.S.*, 1898, **73**, 928.

[34] Konowalow, *Ber.*, 1895, **28**, 1852; *Chem. Soc. Abs.*, 1895, **68** (1), 633.



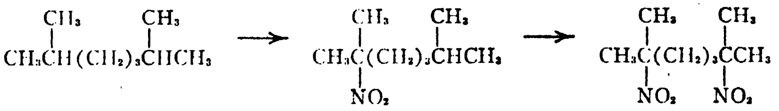
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_2\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3$$

Konowalow[35] has shown that, simultaneously with the formation of tertiary nitro-compounds, there is a slight tendency for nitration to occur in other positions. Under favorable conditions 83 per cent of the mononitro-derivatives of this hydrocarbon consist of the tertiary 2-nitro-compound and 17 per cent of the 1-nitro- and 3-nitro-compounds.

A solid trinitro-compound (melting point 91° C.), derived from diisobutyl, was obtained by Francis and Young[33] by refluxing the hydrocarbon with fuming nitric acid for two days. Markownikow[36] also prepared a solid trinitro-compound, melting point 87°-88° C. (probably identical with the product of Francis and Young) and *4-methyl-3,3,4-trinitropentane* (melting at 95° C.) by the action of nitric acid of specific gravity 1.535.

The nitration of a number of the higher paraffin homologues, including nonane, decane, hendecane and dodecane, by heating with dilute nitric acid has been studied by Worstall.[37] *Nonane* with nitric acid of specific gravity 1.08 gave a 70 per cent yield of mono- and di-nitro-derivatives, and a similar strength acid was used for nitrating *decane*, *hendecane*, and *dodecane*. The nitro-compounds were separated from unaltered hydrocarbons by conversion to their sodium derivatives. These were extracted with water, decomposed by carbon dioxide, and the nitro-compound extracted with ether. Worstall separated the mononitro- from the dinitro-compounds by distillation with steam. Nitrononane was a pale yellow oil, boiling at 215°-218° C. with considerable decomposition. The specific gravities of *nitrononane*, *nitrodecane* and *nitrohendecane* were 0.9227 (17° C.), 0.9105 (15° C.), and 0.9001 (15° C.), respectively.

A number of branched chain higher paraffins have also been nitrated.[38] Thus *2,6-dimethylheptane* is conveniently nitrated at 120° C. with nitric acid of specific gravity 1.075, the chief product being the 2-mononitro-compound. This tertiary nitro-compound is a liquid, boiling point 113°-115° C. at 25 mm., and d_0^0 0.9281. It is readily reduced to the corresponding amine by tin and hydrochloric acid. Further nitration (with acid of specific gravity 1.11) of the mononitro-compound gives the 2,6-dinitro- (or di-tertiary dinitro-) compound, a crystalline solid of melting point 74°-74.5° C. The nitration of this branched chain nonane may be summarized as follows:



$$CH_3\overset{CH_3}{\overset{|}{C}}H(CH_2)_3\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}(CH_2)_3\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}(CH_2)_3\underset{NO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3$$

The nitration of an analogous hydrocarbon, *2,7-dimethyloctane*, has been studied also by Konowalow. By nitrating with concentrated nitric acid the primary nitro-compound is obtained in an almost pure condition.[39] Nitration by dilute nitric acid (specific gravity 1.075) produces a secondary (3- or 4-nitro) and a tertiary (2-nitro) mononitro-compound, and the tertiary dinitro-compound (i.e., *2,7-dinitro-2,7-dimethyloctane*), a crystalline solid of melting point 101.5°-102° C. Konowalow noticed that the nitration of this hydrocarbon was greatly facilitated by the removal of the nitro-compounds as formed and also by using nitric acid recovered from previous nitrations. Aluminum and bismuth nitrates, when heated in an open vessel with these hydrocarbons, nitrate them mainly to primary and secondary (1- and 3-) mononitro-compounds. In the nitration of *2,7-dimethyloctane* (diisoamyl) by dilute nitric acid in a sealed tube, the tertiary nitro-compound is always formed. Concentrated and fuming nitric acid produce oxidation as well as nitration.

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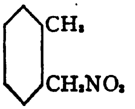
[35] *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 109, 124; *Chem. Soc. Abs.*, 1907, **92** (1), 1.

[36] *Ber.*, 1899, **32**, 1441; *Chem. Soc. Abs.*, 1899, **76** (1), 553.

[37] *Amer. Chem. J.*, 1899, **21**, 210, 218; *Chem. Soc. Abs.*, 1899, **76** (1), 399.

[38] Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 109, 124; *Chem. Soc. Abs.*, 1907, **92** (1), 1; *Chem. Zentr.*, 1906, **2**, 312.

It is interesting to note that the aliphatic side chains in aromatic hydrocarbons may be preferentially nitrated, i.e., without nitration of the aromatic nucleus, by the use of dilute nitric acid. Thus when o-xylene is heated at 110° C. with nitric acid of specific gravity 1.075, nitration of a side chain takes place with the formation of o-tolylnitromethane,[40] a primary nitro-compound readily soluble in alkaline solutions, and possessing the formula



Dilution of the nitrating acid with acetic acid instead of water has the same effect,[41] and, in general, the use of dilute nitric acid and higher temperatures directs the nitration process to the side chains in the benzene homologues. A number of other examples of this phenomenon have been recorded. For example, nitration of durene (*1,2,4,5-tetramethylbenzene*) with benzoyl nitrate leads to nitration of one of the methyl groups.[42] Nitration of *1,2-diphenylpropane*[43] gives the primary nitro-compound of the formula $C_6H_5CH_2CH(C_6H_5)CH_2NO_2$, rather than a nuclear substitution. Similarly, mesitylene gives 1-nitro-1,3,5-trimethylbenzene.[44]

Nitration of Cyclopentane and Cyclohexane Hydrocarbons

Like the paraffins, the five- and six-membered saturated hydrocarbon systems react with nitric acid. Dilute nitric acid at higher temperatures favors the formation of nitro-compounds and more concentrated acid exerts an oxidizing action. Many of the cycloparaffins appear to be nitrated more readily than the corresponding paraffin hydrocarbons. For example, Heusler[45] removed these cyclic hydrocarbons from a crude nonane fraction by dropping the latter into four times its volume of fuming nitric acid. The same method of removing cycloparaffins from paraffin hydrocarbons has been recommended by Ubbelohde,[46] but its general application is doubtful. Of the naphthenes, the cyclopentane homologues seem to be more readily nitrated than the corresponding cyclohexanes. Fuming nitric acid reacts violently with some cycloparaffins at temperatures above 0° C. to form oxidation products.[47] Good yields of dicarboxylic acids may be obtained by the oxidation of cycloparaffins with concentrated nitric acid.

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[39] This appears to confirm the work of Worstall (*loc. cit.*) on the nitration of the normal paraffins by strong acids in an open vessel.

[40] Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 530; *Chem. Soc. Abs.*, 1905, **88** (1), 762.

[41] Konowalow and Gurwitsch, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 537; *Chem. Soc. Abs.*, 1905, **88** (1), 763.

[42] Willstätter and Kubli, *Ber.*, 1909, **42**, 4152.

[43] Konowalow and Dobrowolsky, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 551; *Chem. Soc. Abs.*, 1905, **88** (1), 764. See also, Konowalow and Dobrowolsky, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 547; Konowalow and Jatzewitsch, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 542; *Chem. Soc. Abs.*, 1905, **88** (1), 763.

[44] Konowalow, *Ber.*, 1895, **28**, 1862; *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 256; *Chem. Zentr.*, 1899, 1, 1238.

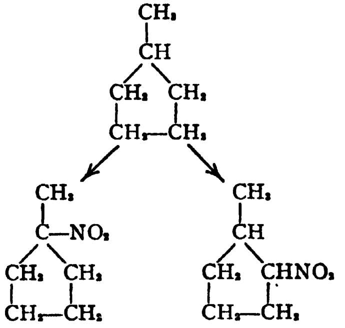
[45] *Ber.*, 1897, **30**, 2747.

[46] Unpublished thesis, Karlsruhe, 1910, 1912. See Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 285.

In the nitration of the cycloparaffin hydrocarbons, primary, secondary, and tertiary nitro-compounds are formed, though the latter usually constitute the main product, whenever possible.

The nitration of a *cyclopentane* fraction of Caucasian petroleum, boiling point 50°-51° C., is reported by Markownikow [48] to yield a secondary nitro-compound as well as a large proportion of glutaric acid. No details of the conditions of nitration were supplied by Markownikow but, in all probability, fairly strong nitric acid was employed. The nitrocyclopentane was readily reduced to an amine.

The nitration of *methylcyclopentane* has been investigated. Fuming nitric acid of specific gravity 1.55 acts only slowly on this hydrocarbon if the temperature is kept low, but at temperatures above 0° C. a violent reaction takes place with the production of acetic acid, carbon dioxide, and other oxidation products. Nitrosulphuric acid is without action on this hydrocarbon in the cold.[49] Methylcyclopentane can be nitrated at 115° to 120° C. by nitric acid of specific gravity 1.075 to yield,[50] as the main product, the tertiary nitro-compound, *1-nitro-1-methylcyclopentane*. An isomeric secondary nitro-compound, *2-nitro-1-methylcyclopentane,* is simultaneously formed,[49, 51] and may be separated from the tertiary compound by means of its solubility in aqueous alkali. Both nitro-compounds are readily reduced to the corresponding amines by tin and hydrochloric acid. Succinic and α-methylglutaric acids are also formed during the nitration of the hydrocarbon. The nitration of methylcyclopentane may be summarized as follows:



tertiary nitro-compound, b.p. 92° C. at 40 mm. *secondary nitro-compound,* b.p. 99° C. at 40 mm.

From the products of the action of nitric acid (of sp. gr. 1.38) upon a fraction of Caucasian petroleum, boiling between 95° and 100° C., Beilstein and Kurbatow [52] isolated a compound, $C_6H_{11}NO_2$, boiling at 210° to 215° C. This compound is identical with nitrocyclohexane, later investigated and described by Markownikow.[53]

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[47] Markownikow, *Ann.*, 1899, **302**, 15; *Chem. Soc. Abs.*, 1899, **76** (1), 22; *Ann.*, 1899, **307**, 335; *Chem. Soc. Abs.*, 1899, **76** (1), 799.

[48] *Ber.*, 1897, **30**, 974; *Chem. Soc. Abs.*, 1897, **72** (1), 329.

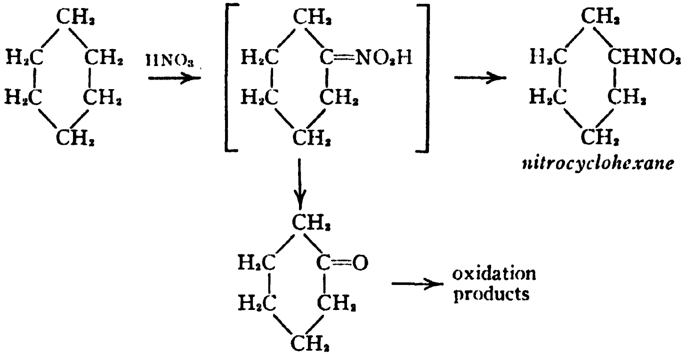
[49] Markownikow, *Ann.*, 1899, **307**, 335; *Chem. Soc. Abs.*, 1899, **76** (1), 799; *Ber.*, 1895, **28**, 1236. *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 214; *Chem. Zentr.*, 1899, 1, 1211.

[50] The nitration of methylcyclopentane can also be effected by dilute nitric acid at 100° C. according to Kishner, *J. prt. Chem.*, 1897, **56** (2), 369.

[51] See Nametkin, *J. Russ. Phys.-Chem. Soc.*, 1911, **43**, 1603; *Chem. Soc. Abs.*, 1912, **102** (1), 175.

[52] *Ber.*, 1880, **13**, 1818; *Chem. Soc. Abs.*, 1881, **40**, 159.

Cyclohexane is practically unaffected by the usual nitrating mixture of nitric and sulphuric acids (nitrosulphuric acid) in the cold, while it is oxidized by concentrated nitric acid with the production of adipic acid. The hydrocarbon may be successfully nitrated[54] by Konowalow's method, using dilute nitric acid at temperatures above 100° C. The product is *nitrocyclohexane,* a colorless liquid of boiling point 109.5° C. at 40 mm., and d^0_0 1.0853.[55] According to Nametkin,[56] this nitro-compound is not an intermediate compound in the oxidation of cyclohexane by nitric acid to adipic acid since the latter is formed from cyclohexane more readily than from the nitro-derivatives. Nametkin considers that the intermediate compound in the oxidation reaction is an unstable isonitrocyclohexane which is immediately converted partly into the stable nitrocyclohexane, and partly into an aldehyde (or ketone, according to the nature of the hydrocarbon). The latter product then undergoes further oxidation to the corresponding acid. The application of Nametkin's mechanism to the case of cyclohexane may be represented as follows:



Nametkin[56] has shown that the nitration of cyclohexane can be carried out by using, instead of nitric acid, fused aluminum nitrate, $Al(NO_3)_3.9H_2O$, as the nitrating agent. At temperatures above its melting point, this salt supplies an equilibrium concentration of nitric acid which is maintained constant at any particular temperature as long as any unhydrolyzed nitrate remains in the system. By heating cyclohexane at 115° to 120° C. with about 3 parts by weight of aluminum nitrate a considerably greater yield (i.e., 56 per cent) of mononitrocompound was obtained than when dilute nitric acid was used as the nitrating medium. Cyclohexanone, possibly a nitrocyclohexanone, and a dinitrodicyclohexyl (melting point 216.5°-217° C.) were produced, in addition to mononitrocyclohexane, by this method of nitration.

Methylcyclohexane is vigorously oxidized by fuming nitric acid and acid of lower concentration both nitrates and oxidizes it. The hydrocarbon is scarcely affected by nitrosulphuric acid at 70° C. in sealed tubes or at 80° C. in open vessels.[57] Nitration of this hydrocarbon by acid of specific gravity 1.2, produces three isomeric mononitro-compounds, including a primary, secondary, and a tertiary product, with about a 58 per cent yield. Nametkin[58] found that the yield of nitration products may be increased to 72 per cent by the use of fused aluminum nitrate as a nitrating agent. The constitution and physical constants of the three mononitro-compounds are as follows:

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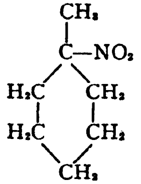
[53] *Ann.*, 1898, **302**, 15; *Chem. Soc. Abs.*, 1899, **76** (1), 22.

[54] Markownikow, *Ann.*, 1898, **302**, 15; *Chem. Soc. Abs.*, 1899, **76** (1), 22.

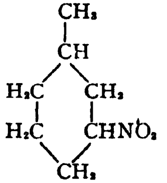
[55] *J. Russ. Phys.-Chem. Soc.*, 1908, **40**, 1570; *Chem. Soc. Abs.*, 1909, **96** (1), 93; *Ber.*, 1909, **42**, 1372.

[56] *J. Russ. Phys.-Chem. Soc.*, 1910, **42**, 581; *Chem. Soc. Abs.*, 1910, **98** (1), 829.

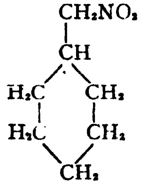
[57] Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1903, **35**, 1033; *Chem. Zentr.*, 1904, **1**, 1345; *Ann.*, 1905, **341**, 130.



tertiary nitro-compound
(b.p. 109°-110° C.
at 40 mm.)



secondary nitro-compound
(b.p. 119°-120° C.
at 40 mm.)

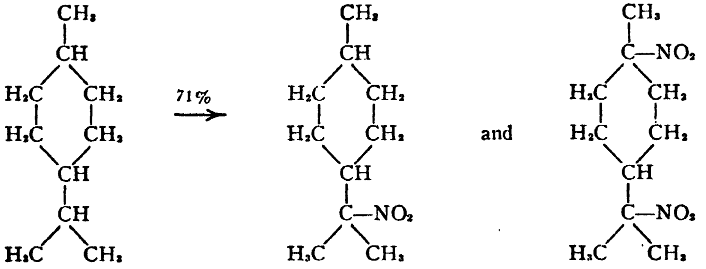


primary nitro-compound
(b.p. 98° C. at 10 mm.)

The tertiary nitro-compound, which may be separated from the isomeric primary and secondary products by the solubility of the two latter in aqueous alkalies, may be readily reduced to an amine by tin and hydrochloric acid.

Little is known of the nitration products of the homologues of cyclohexane. Nitration products boiling between 123° and 126° C. were obtained by Putochin[59] by the action of nitric acid on an isooctanaphthene, C_8H_{16}, of unknown configuration from a fraction of Caucasian petroleum boiling between 122° and 125° C. *1,2,4-Trimethylcyclohexane* can be nitrated by heating with five times its volume of dilute nitric acid (sp. gr. 1.075) in a sealed tube at 120°-130° C. The products consist of a mixture of secondary and tertiary nitro-compounds, readily separated by the usual means.[60] The tertiary nitro-compound, described as a colorless liquid boiling at 128°-130° C. at 40 mm., is reduced by zinc and acetic acid to yield an amine and a ketone.

When *p-menthane* is nitrated by dilute nitric acid (sp. gr. 1.075) at 110° C., a mixture of mononitro-compounds is formed consisting of about 71 per cent of tertiary compound and 29 per cent of primary and secondary products. A tertiary dinitro-compound is also produced.[61] The nitration of p-menthane may be represented as follows:



tertiary mononitro-compound

tertiary dinitro-compound

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[58] *J. Russ. Phys.-Chem. Soc.*, 1910, 42, 691; *Chem. Soc. Abs.*, 1910, 98 (1), 830.

[59] See Markownikow, *J. Russ. Phys.-Chem. Soc.*, 1884, 16, 296; *Ber.*, 1885, 18, Ref. 186.

[60] Konowalow, *J. Russ. Phys.-Chem. Soc.*, 1893, 25, 390; *Ber.*, 1893, 26, Ref. 878; *Chem. Soc. Abs.*, 1894, 66 (1), 159.

[61] Konowalow and Jebenko, *J. Russ. Phys.-Chem. Soc.*, 1899, 31, 1027; *Chem. Soc. Abs.*, 1900, 78 (1), 324; *J. Russ. Phys.-Chem. Soc.*, 1906, 38, 449; *Chem. Soc. Abs.*, 1907, 92 (1), 203.

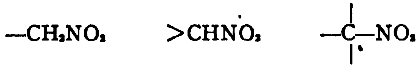
Both the tertiary mono- and di-nitro-derivatives may be readily reduced to the corresponding amines.

The nitration of a *dimethylethylcyclohexane* by dilute nitric acid (sp. gr. 1.075) at 120° to 125° C. was investigated by Markownikow and Rudewitsch.[62] The product is a mixture of tertiary and secondary nitro-compounds, both of which are readily reduced to the corresponding amines by tin and hydrochloric acid. Nitration of this decanaphthene at water-bath temperature by nitric acid of specific gravity 1.41 also resulted in the production of mono- and di-nitro-compounds.

Engler and Halmai[63] nitrated a nonanaphthene fraction boiling at 132° to 137° C. from a cylinder oil from Baku. They obtained a mononitrononanaphthene boiling with decomposition at 220° to 226° C. and having a specific gravity at 18° C. of about 1.02. The configuration of this compound was not determined. They also nitrated a decanaphthene fraction from the same source having a boiling range of 158° to 165° C. The mononitrodecanaphthene, $C_{10}H_{19}NO_2$, formed had a specific gravity of 1.0354 at 18° C. and boiled at 112°-120° C. at 12 mm. This compound was identical with the tertiary nitro-compound obtained earlier by Engler and Routala[64] on nitrating a decanaphthene found in the products of polymerization of amylene with aluminum chloride. Steinkopf and Freund[65] also isolated what appeared to be this same compound on nitrating a fraction (b.p. 165°-172° C.) of turpentine cracked with aluminum chloride.

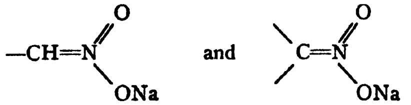
PROPERTIES OF NITRO-COMPOUNDS OF PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

Three main types of nitro-compounds exist, namely, primary, secondary, and tertiary compounds having the following characteristic groupings:



$-CH_2NO_2$ *primary* $>CHNO_2$ *secondary* $-\overset{|}{\underset{|}{C}}-NO_2$ *tertiary*

The first two are soluble in aqueous (or alcoholic) alkali solutions, in which the tertiary compounds are insoluble. This solubility is associated with the conversion of primary and secondary nitro-compounds into the tautomeric acidic form, the alkali salts of which probably possess the structures,[66]



primary pseudo-acid form and *secondary pseudo-acid form*

From a practical standpoint, the primary and secondary nitro-compounds are readily differentiated by their behavior towards nitrous acid. When a primary nitro-compound is treated with an alkaline solution of sodium nitrite, and the resulting solution just acidified, a nitrolic acid is formed, the alkali salts of which are red in solution. Under similar circumstances secondary nitro-compounds furnish pseudonitroles, which are blue in solution. These reactions are represented as follows:

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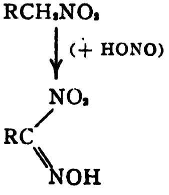
[62] *J. Russ. Phys.-Chem. Soc.*, 1893, 25, 385; 1898, 30, 586; *Chem. Soc. Abs.*, 1899, 76 (1), 581.

[63] *Ber.*, 1910, 43, 397; *Chem. Abs.*, 1910, 4, 1167.

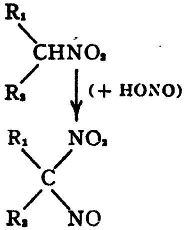
[64] *Ber.*, 1909, 42, 4613; *Chem. Soc. Abs.*, 1910, 98 (1), 2.

[65] *Ber.*, 1914, 47, 411; *Chem. Soc. Abs.*, 1914, 106 (1), 304.

[66] Nef, *Ann.*, 1892, 270, 331; 1894, 280, 263; *Chem. Soc. Abs.*, 1895, 68 (1), 3. Some of the primary nitro-compounds of the higher paraffins are only slowly soluble in aqueous potassium hydroxide (Worstall, *Amer. Chem. J.*, 1899, 21, 210, 218; *Chem. Soc. Abs.*, 1899, 76 (1), 399).

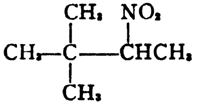


nitrolic acid



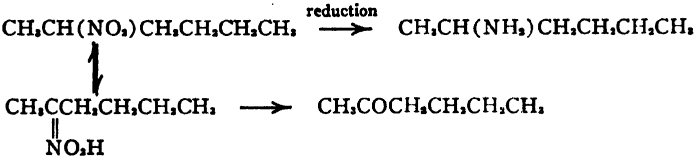
pseudonitrole

The mononitro-compounds of paraffins and cycloparaffins are usually colorless liquids of fairly high boiling point. Some of the dinitro- and a few trinitro-compounds are crystalline solids. While tertiary mono- and di-nitro-compounds are very readily reduced by tin and hydrochloric acid, for example, to the corresponding mono- and di-amines, the primary and secondary nitro-compounds are reduced to the oxime of the corresponding ketone or aldehyde, evidently by reduction of the pseudo-acidic form of the nitro-compound. The relative proportions of the products (i.e., amine or ketone) depend to some extent upon the conditions of reduction. Thus, Markownikow[67] noted that the secondary nitro-compound of trimethylethylmethane, having the formula



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle NO_2}{C}HCH_3$$

is readily reduced to the corresponding secondary amine by tin and hydrochloric acid. Reduction by alkaline stannous chloride, on the other hand, yields an oxime which can be hydrolyzed to a ketone. According to Konowalow,[68] reduction of the secondary nitro-compounds of n-hexane by zinc and acetic acid yields a mixture of β-hexylamine and methyl butyl ketone. These reactions may be represented in the following manner:



The primary nitro-compounds derived from n-hexane and octane, described by Worstall,[69] appear to be quite readily reduced to the corresponding primary amines. On the other hand, the primary nitro-compound of 2,7-dimethyloctane (i.e., 1-nitro-2,7-dimethyloctane) prepared by Konowalow,[70] was reduced by tin and hydrochloric acid to a mixture of the corresponding primary amine and the aldehyde, $CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH(CH_3)CHO$. The secondary nitro-compound of the same hydrocarbon (3- or 4-nitro-2,7-dimethyloctane) is reduced under similar circumstances to the corresponding secondary amine together with a small amount of a ketone, boiling point 190°-192° C.

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[67] *Ber.*, 1899, 32, 1445; *Chem. Soc. Abs.*, 1899, 76 (1), 554.

[68] *J. Russ. Phys.-Chem. Soc.*, 1894, 25, 472; *Chem. Soc. Abs.*, 1894, 66 (1), 265.

[69] *Amer. Chem. J.*, 1898, 20, 202; *Chem. Soc. Abs.*, 1898, 74 (1), 346.

[70] *J. Russ. Phys.-Chem. Soc.*, 1906, 38, 109, 124; *Chem. Soc. Abs.*, 1907, 92 (1), 1.

The tertiary nitro-derivatives of cyclopentane and cyclohexane homologues are also easily reduced to the corresponding amines, though some of the secondary compounds yield only derivatives of the corresponding ketone. Thus, nitrocyclohexane, on reduction with tin and hydrochloric acid, gives cyclohexanone and its condensation products. On the other hand, both the tertiary and secondary nitromethylcyclopentanes are converted largely to the corresponding amines on reduction with tin and hydrochloric acid.[71]

NITRO-COMPOUNDS OF PETROLEUM AND THEIR APPLICATIONS

Frasch[72] produced a brown powdered dyestuff by nitrating crude petroleum, its distillates, or residues. The petroleum is subjected to the action of a mixture of 3 parts of sulphuric and 1 part of nitric acids until all the aromatic hydrocarbons, olefins, naphthenes, and unsaturated hydrocarbons in the oil are taken up in the acid mixture. The acid layer, which contains the aromatic hydrocarbons and tarry substances, is allowed to separate and is withdrawn. This acid mixture is then heated at 60° to 80° C. to effect conversion of the hydrocarbons to nitro- and oxidized products. The free acid is removed by washing with cold water. The soluble nitro-compounds are extracted with water and neutralized with calcium carbonate or oxide, which converts the nitro-compounds into soluble and insoluble calcium salts. The insoluble calcium salts are separated by filtration and may be converted to soluble salts by reaction with sodium, potassium, or ammonium carbonate. The soluble dyestuff thus formed is precipitated from the solution by the addition of hydrochloric acid or sodium chloride. This is a brown resinous material which can be pulverized. It is only slightly soluble in cold water but readily soluble in hot water, acetone, and glycerol. The solution of the soluble calcium salt, obtained in the above procedure, may be treated[73] with hydrochloric acid or sodium chloride to precipitate a soluble yellow or reddish-brown dye which can be applied to silk or wool. Nitro-compounds of "petrocenes", the high-boiling hydrocarbons found in the redistillation of petroleum residues (see Chapter 6), have been described by Zaloziecki and Gans.[74]

Petroleum distillates, boiling between 270° and 380° C. and of specific gravity 0.87 to 0.96, were nitrated by Edeleanu and Filiti[75] with a mixture of concentrated nitric and sulphuric acids. The products were precipitated from the acid by the addition of water. The distillates, before nitration, can be freed from resinous materials by treatment with small quantities of sulphuric acid. These nitro-compounds, they stated, could be used as substitutes for camphor in the manufacture of celluloid and in the preparation of lacquers, varnishes, and brown to black substantive dyes. Freund[76] treated various Borislaw petroleum fractions in this way. He nitrated 1 part of the distillates with 3 parts of a mixture of concentrated nitric and sulphuric acids. Yellow or reddish-brown powders containing from 6.8 to 8.5 per cent of nitrogen were obtained. A brown powder containing 6.80 per cent nitrogen and corresponding to the formula $C_{11}H_{17}NO_2$ was one of these products. Brown substantive dyes could be made by heating these with alkalies.[77] Freund also prepared brown to violet-brown sulphur dyes by heating these nitro-compounds with sulphur and alkalies.

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[71] Nametkin, *J. Russ. Phys.-Chem. Soc.*, 1911, **43**, 1603; *Chem. Soc. Abs.*, 1912, **102** (1), 175.

[72] U. S. Patent 519,036, May 1, 1894; assigned to Grasselli Chemical Co.; *Chem. Ztg.*, 1895, 831. German Patent 84,626, 1893; *Chem. Zentr.*, 1896, 1, 1040.

[73] U. S. Patent 518,989, May 1, 1894; assigned to Grasselli Chemical Co.; German Patent 84,626, 1893; *Z. angew. Chem.*, 1896. **9**, 89; *Chem. Ztg.*, 1896, 94.

[74] *Chem. Ztg.*, 1900, **24**, 553; *Chem. Soc. Abs.*, 1900, **78** (1), 593.

[75] British Patent 9,416, 1902; *J.S.C.I.*, 1903, **22**, 621. German Patent 154,054, 1902; *Chem. Zentr.*, 1904, **2**, 1177. French Patent 320,618; Austrian Patent 23,571. *Bull. soc. chim.*, 1900, **23** (3), 382. See also U. S. Patent 745,802, Dec. 1, 1903, and Edeleanu, *Compt. rend. du II congres de pétrole à Liège*, 1905; *Naphtha*, 1905, **13**, 299.

[76] *Z. angew. Chem.*, 1912, **25**, 1058; *Chem. Abs.*, 1912, **6**, 2520.

The nitration of high-boiling American and Russian petroleum fractions dissolved in an equal volume of benzine was carried out by Marcusson.[78] By treating such solutions with three volumes of nitric acid (specific gravity 1.52) characteristic yellow dinitro-compounds, containing from 6.5 to 7.5 per cent of nitrogen, were obtained. These were slightly soluble in petroleum ether, partially soluble in alcohol, and dissolved completely in acetone or benzene. Their potassium salts, made by warming the nitro-compounds with alcoholic potassium hydroxide solution and evaporating the alcohol, were dark-brown in color and soluble in water; the original nitro-compounds were insoluble in water.

Although the nitration of aromatic fractions of petroleum is outside the scope of this book, nevertheless the importance of these compounds deserves at least cursory mention. The production of TNT from toluene-containing fractions has already been stressed in Chapter 1. Mizuta[79] prepared mono- and di-nitrotoluenes in good yield from aromatic fractions of Japanese gasolines. The relative yields of secondary and tertiary nitro-derivatives obtained on nitration led Nametkin and Nifontova[80] to believe that paraffin wax contains about 25 to 30 per cent of isoparaffins. From a Grozny and an American paraffin wax they obtained a tertiary nitrate ($C_{24}H_{49}NO_2$) melting at 29° C., a secondary nitrate ($C_{24}H_{49}NO_2$) melting at 45° to 48° C., and an oil consisting of a dinitrate ($C_{24}H_{48}(NO_2)_2$).

Forrest and Meigs[81] obtained resins by treating a distillate from the destructive distillation of asphalt, asphaltic petroleum or materials such as gilsonite with nitric acid of specific gravity 1.42. Because of the great reactivity of the unsaturated bodies formed in the destructive distillation of these carbonaceous materials the addition of nitric acid must be made with caution. Forrest and Meigs recommended that the volume of acid added to the oil at any one time never be more than 1 part to 2500 parts of oil. In carrying out the preparation, the oil is heated to about 93° C. and the temperature during the reaction is maintained below 104° C. The reaction is stopped when 1 part by volume of acid has been added to 2 parts by weight of the oil. Light yellow semi-solids are obtained, the hardness of which depends upon the hydrocarbon fraction used. With a fraction boiling between 204° and 316° C., for example, a resin of medium hardness was formed. A lower-boiling fraction from the decomposition of gilsonite gave a viscous oil similar in properties to nitrated castor oil. These nitro-resins have been suggested as additions to pyroxylin compounds, for example, in the preparation of lacquers, leather dressings, and artificial leather.

Similar resinous products have also been obtained by treating related materials with nitric acid.[82] In this manner Day,[83] for example, used powdered gilsonite, grahamite, and albertite. Tar mixtures also were used by Flexer[84] in making a material resembling asphalt.

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[77] See Edeleanu and Filiti, German Patent 159,428, 1902; *Chem. Zentr.*, 1905, **1**, 1199.

[78] *Chem. Ztg.*, 1911, **35**, 742.

[79] *J. Soc. Chem. Ind., Japan*, 1932, **35**, Suppl. binding 519; *ibid.*, 1933, **36**, Suppl. binding 117-118; *Chem. Abs.*, 1933, **27**, 1492, 2792. The mechanism of nitration of benzene has been discussed by Tronov and Laduigina, *Ukrain. Khem. Zhur.*, 1932, **7** (1), 55; *Chem. Abs.*, 1933, **27**, 1620. Manufacture of aromatic nitro-compounds from petroleum is described by Ihrig, U. S. Patent 1,838.311, Dec. 29, 1931; *Brit. Chem. Abs.* **B**, 1932, 1072.

[80] *J. Appl. Chem., Russia*, 1933, **6**, 248; *Brit. Chem. Abs.* **B**, 1933, 692.

[81] U. S. Patent 1,305,790, June 3, 1919; assigned to Barber Asphalt Paving Co.; *Chem. Abs.*, 1919, **13**, 2140.

[82] For a more complete and detailed discussion of these nitro-resins see Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog Co., Inc., New York, 1923, 320.

[83] U. S. Patent 967,337, Aug. 16, 1910; *Chem. Abs.*, 1910, **4**, 3015.

Charbonneaux[85] nitrated various hydrocarbon oils, particularly California crude oils, with 5 to 10 per cent of concentrated nitric acid. Several layers were formed on cooling, one of which consisted of a heavy tarry substance insoluble in nitric acid and alcohol, while another was a brown sticky material also insoluble in nitric acid but soluble in alcohol. These substances, which are both nitrated and oxidized products, can be incorporated in liquid fuels. For example, 1 to 3 parts of the resin are added to 100 parts of alcohol and 20 parts of ether.

The preparation of a motor fuel containing amino-compounds and of high anti-detonating properties has been described by Ellis.[86] The distillates obtained by cracking the higher-boiling petroleum fractions under pressure are subjected to the action of concentrated nitric acid and the nitro-compounds thus formed are subsequently reduced by the action of iron and dilute sulphuric acid. Nitration and purification of the distillate may be simultaneously effected by employing a mixture of nitric and sulphuric acids. In addition to acid reduction with metals such as iron, alkaline reduction by zinc or aluminum and a solution of sodium hydroxide is also effective.

The nitration of an *octane fraction of petroleum* to furnish a crude mononitro-compound capable of being used as a solvent for cellulose derivatives and resins, has been described by Hopkins.[87] Fourteen hundred parts of an octane fraction of petroleum, boiling range 125° to 130° C., are mixed with 1000 parts of 94 per cent aluminum nitrate[88] and 600 parts of 68 per cent nitric acid and the mixture heated to 130° to 140° C. in an oil bath. Hydrocarbon, nitric acid, and water distil off and the hydrocarbon is condensed and returned to the mixture. The resulting 950 parts of reaction mixture are steam-distilled, yielding 370 parts of crude mononitro-compound, and 580 parts of unchanged hydrocarbon.

The nitration of non-benzenoid substances, such as petroleum fractions which contain hydrocarbons having from six to twelve carbon atoms, yield materials which can be mixed with alcohols and benzene to form solvents for nitrocellulose.[88a] Nitrated products lower the ignition and flash points of petroleum distillates. The compounds used for this purpose are obtained by the nitration of aromatic hydrocarbons such as benzene or toluene, or by the nitration and distillation of kerosene distillates.[88b]

ACTION OF NITROSYL CHLORIDE AND CHROMYL CHLORIDE ON SATURATED HYDROCARBONS

The photochemical reaction of nitrosyl chloride with n-heptane (from *Pinus jeffreyi*) has been investigated by Lynn and Hilton[89] with the following results: Pure heptane was saturated with nitrosyl chloride and the resultant reddish-brown solution, though unchanged in the dark for weeks, gradually became blue under the influence of sunlight. Simultaneously with the appearance of the blue color, which was probably caused by the production of a nitroso-compound, ammonium chloride was deposited. The blue color quickly disappeared spontaneously and the resulting turbid liquid gradually deposited a yellow oil which sank to the bottom of the container and evolved a yellow gas containing 75 per cent hydrogen chloride and 2.5 per cent nitric oxide. Fifty grams of this oil were steam-distilled, yielding much hydrogen chloride together with 30 grams of an oil having a fragrant odor, and some hydroxylamine. From the boiling points and refractive indices of the fractions obtained by distilling this oil, it was concluded that it contained a mixture of three ketones—methyl amyl ketone, dipropyl ketone, and ethyl butyl ketone, derived from the heptane, with a preponderating proportion of the dipropyl ketone. The production of this latter ketone and its oxime was subsequently substantiated. The following reactions were believed to take place:

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[84] Austrian Patent 74,127; *Kunststoffe,* 1921, 2, 12; German Patent 332,634, 1918; *J.S.C.I.*, 1921, 40, 349A.

[85] U. S. Patent 1,480,372, Jan. 8, 1924; *Chem. Abs.*, 1924, 18, 895.

[86] U. S. Patent 1,867,814, July 19, 1932; assigned to Ellis-Foster Company.

[87] U. S. Patent 1,588,027, June 8, 1926; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1926, 721.

[88] The use of aluminum nitrate in the nitration of saturated hydrocarbons (e.g., cyclohexane) has been described by Konowalow (*loc. cit.*, 1906), and Nametkin (*J. Russ. Phys.-Chem. Soc.*, 1910, 42, 581; *Chem. Soc. Abs.*, 1910, 98 (1), 829).

[88a] Hopkins and Buc, U. S. Patent 1,694,097, Dec. 4, 1928; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1929, 366.

[88b] Wingett, U. S. Patent 1,185,747, June 6, 1916; *J.S.C.I.*, 1916, 35, 828.

[89] *J.A.C.S.*, 1919, 41, 368; 1922, 44, 645; see also, Kremers, *J. Amer. Pharm. Assoc.*, 1920, 9, 857.

$$\begin{aligned} &C_7H_{16} + NOCl \longrightarrow C_7H_{15}NO \text{ (blue)} + HCl \\ &C_7H_{15}NO \text{ (blue)} \longrightarrow C_7H_{14}{=}NOH \text{ (oil)} \\ &C_7H_{14}{=}NOH + H_2O \longrightarrow C_7H_{14}O + NH_2OH \end{aligned}$$

The reaction therefore proceeds through the intermediate production of a blue nitroso-compound which then isomerizes to the oxime of a ketone. Hydrolysis of this oxime yields the free ketone. Lynn and Hilton found, by experiments with ultraviolet radiation and working at different temperatures, that the formation of the blue nitroso-compound takes place both in sunlight and in ultraviolet light at temperatures up to 80° C. For some reason, however, the less refrangible rays are necessary to effect the conversion of the nitroso-compound into the oxime.

Recent work by Kester, Looker, and Hass[90] on the action of nitrosyl chloride with butane both in the liquid and gaseous phases and under the influence of sunlight, artificial light, heat, and catalysts has demonstrated that at least three types of reactions take place: (1) Chlorination, which is the predominating reaction. Polychlorides prevail over the monochlorides among the products. (2) Oxidation. Notable proportions of fatty acids are formed in this reaction, the principal one being butyric, though propionic and acetic in measurable quantities were also obtained and the presence of formic was indicated. (3) Nitrosation. No oxime of either butyraldehyde or methyl ethyl ketone was isolated and identified but methyl ethyl ketone itself was found in both the upper and lower layers of the reaction product. The amounts of it, however, were at all times small.

The lower layer of the reaction product consisted in the main of strong aqueous hydrochloric acid saturated with ammonium chloride in addition to such water-soluble ingredients as methyl ethyl ketone, fatty acids, and doubtless other unidentified products in small amounts. Ammonium chloride precipitated during the course of the reaction, together with small amounts of hydroxylamine hydrochloride, which was isolated. The upper layer contained unreacted butane, chlorobutanes, methyl ethyl ketone, and fatty acids in addition to small proportions of by-products not identified. The presence of lacrimatory substances was very noticeable. They may have been, and probably were, chlorinated ketones.

The action of *chromyl chloride*, CrO_2Cl_2, on alkylbenzenes has been studied. The reaction, investigated by Etard[91] and by Miller and Rohde,[92] yields oxygenated derivatives. In general, the methylbenzenes produce the corresponding aldehydes, while hydrocarbons with longer side chains usually yield ketones and, in some cases, the corresponding aldehyde. Thus ethylbenzene and chromyl chloride yield acetophenone and an oil which combines with sodium hydrogen sulphite and probably consists of phenylacetaldehyde and benzaldehyde. Similarly p-cymene is oxidized by chromyl chloride to an aldehyde and a ketone, p-tolyl ethyl ketone.

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[90] Private communication from E. B. Kester.

[91] *Ann. chim. phys.*, 1881, 22 (5), 218; *Chem. Soc. Abs.*, 1881, 40, 581.

[92] *Ber.*, 1890, 23, 1070; *Chem. Soc. Abs.*, 1890, 58, 978.

Little work has been reported on the action of chromyl chloride on non-benzenoid hydrocarbons, but, here again, oxidation to ketones also appear to take place. Etard [93] obtained a chloroketone by the action of this reagent on hexane, and Schulz [94] subjected a number of light Boryslaw petroleum fractions to the action of chromyl chloride and obtained a mixture of ketones, which were not identified.

APPLICATION OF FRIEDEL-CRAFTS REACTIONS TO PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

One of the most interesting and important developments in the chemistry of the saturated non-benzenoid hydrocarbons is the application of the Friedel-Crafts reaction not only to cycloparaffins, such as cyclopentane and cyclohexane, but also to straight chain paraffins. Formerly such reactions were considered to apply solely to aromatic substances. The investigation of the catalytic effects of metallic halides on the saturated non-benzenoid hydrocarbons is still in the initial stages. The evidence available definitely indicates, however, that changes are effected with non-benzenoid hydrocarbons by these reagents but not nearly as readily as with aromatic compounds. The importance of these reactions lies in the possibility of converting saturated hydrocarbons directly into ketones by reaction with acid chlorides, or with carbon monoxide under pressure, in the presence of aluminum chloride.

The fact that some naphthenes are capable of undergoing certain types of Friedel-Crafts condensations appears to have been noticed as early as 1899 by Zelinski.[95] He reported the production of various ketones by treatment of fractions of Baku gasoline (rich in cycloparaffin hydrocarbons) with acetyl chloride in the presence of aluminum chloride. For example, two isomeric ketones of the formula $C_6H_{11}COCH_3$ (presumably derivatives of cyclohexane and methylcyclopentane, respectively) were obtained in this way from the fraction of Baku gasoline of boiling point 80°-82° C. Similarly, ketones of the formulas $C_7H_{13}COCH_3$ and $C_8H_{15}COCH_3$ were prepared from the fractions boiling at 100°-102° C. and 119°-120° C., respectively. Marcusson and Vielitz [96] proposed a method of removing naphthenes from paraffins by treating the mixture with benzoyl chloride in the presence of anhydrous aluminum chloride. According to Marcusson, the naphthenes were attacked but not the paraffins. In view of later work, however, sharp separation of cycloparaffin and paraffin hydrocarbons is not attained by this procedure.

An example of the reaction of hydrogen atoms not attached to an aromatic nucleus under the influence of Friedel-Crafts condensing agents has been described by von Braun and his associates.[97] When 5-phenyl-1-chloropentane is treated, in light petroleum or carbon disulphide solution, with anhydrous aluminum chloride, elimination of hydrogen chloride takes place and there is a considerable formation of phenylcyclopentane. The reaction may be represented as follows:

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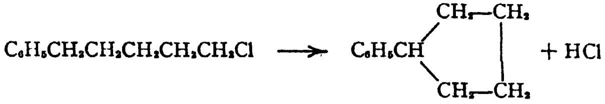
[93] *Ber.*, 1877, **10**, 236; *Ann. chim. phys.*, 1881, **22** (5), 282; *Chem. Soc. Abs.*, 1881, **40**, 581.

[94] *Petroleum*, 1910, **6**, 189; *Chem. Abs.*, 1911, **5**, 587.

[95] *J. Russ. Phys.-Chem. Soc.*, 1899, **31**, 402; *Bull. soc. chim.*, 1899, **22** (3), 870. See also, *J. Russ. Phys.-Chem. Soc.*, 1905, **37**, 632; *Bull. soc. chim.*, 1907, **2** (4), 1122.

[96] *Chem. Ztg.*, 1913, **37**, 552; *Chem. Soc. Abs.*, 1913, **104** (1), 581.

[97] von Braun and Deutsch, *Ber.*, 1912, **45**, 1267. von Braun and Kühn, *Ber.*, 1927, **60B**, 2557. von Braun, *Ber.*, 1931, **64B**, 2869.



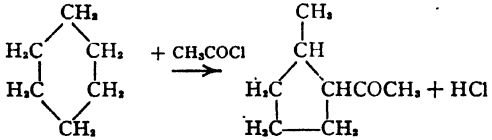
In the same way 5-p-tolyl-1-chloropentane condenses to yield some p-tolylcyclopentane.

Perhaps the most striking work on the preparation of ketones from paraffin and cycloparaffin hydrocarbons by the Friedel-Crafts reaction is that of Hopff,[98] a review of which is to be found in Chapter 18. It is sufficient to state here that both paraffin and cycloparaffin hydrocarbons were condensed with acid chlorides (acetyl chloride) and also with carbon monoxide under high pressure in the presence of anhydrous aluminum chloride to yield ketones and other substances. From *n-pentane* and acetyl chloride, the main product was 2-acetylpentane, while *cyclohexane* yielded a cycloalkyl ketone. In the presence of aluminum chloride, carbon monoxide under high pressure could be made to react with saturated hydrocarbons at temperatures of about 100°C. to give ketones. Although the yields of pure ketones obtained by Hopff in these reactions were rather poor and considerable quantities of other substances were formed, the work of this investigator is of importance to those interested in the chemical transformation of saturated hydrocarbons.

Acetyl chloride reacts slowly with cyclohexane in the presence of aluminum chloride.[99] On standing, the reaction products separate into two layers; the upper consisting of the hydrocarbons, $C_{12}H_{12}$ and $C_{18}H_{22}$, and the lower, on decomposition with water, yielding a ketone of the formula $C_8H_{14}O$. This ketone was not methyl cyclohexyl ketone, but was identified as *1-methyl-2-acetyl-cyclopentane.* In a similar manner butyryl and benzoyl chlorides formed, in addition to hydrocarbons, the corresponding *1-methyl-2-butyryl-* and *1-methyl-2-benzoyl-cyclopentanes,* respectively. In the latter case the lower, or ketone, layer contained a large proportion of benzaldehyde from the reduction of the benzoyl chloride. The above results can be explained on the bases of the following reactions:

(a) Condensation of cyclohexane to higher hydrocarbons ($C_{12}H_{22}$) containing a lower hydrogen content with simultaneous reduction of the acid chloride to aldehyde; and

(b) Direct combination of the acid chloride with cyclohexane, accompanied by the elimination of hydrogen chloride and simultaneous rearrangement of the cyclohexane ring, under the influence of aluminum chloride, to give the 2-derivative of 1-methylcyclopentane.[100] The latter process may be represented as follows:



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[98] *Ber.,* 1931, **64,** 2739; 1932, **65,** 482. See also, U. S. Patent 1,801,350, April 21, 1931; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.,* 1931, **25,** 3358.

[99] Nenitzescu, Isacescu and Ionescu, *Ann.,* 1931, **491,** 189, 210; *Brit. Chem. Abs.* **A,** 1932, 49. Substantiation of the work of Nenitzescu and Ionescu on the condensation of cyclohexane with acetyl chloride is provided by Unger (*Ber.,* 1932, **65B,** 467) and by Hopff (*Ber.,* 1932, **65B,** 482).

[100] The rearrangement of cyclohexane to methylcyclopentane takes place under the influence of aluminum chloride. See Aschan, *Ann.,* 1902, **324,** 1; *Chem. Soc. Abs.,* 1902, **82** (1), 749.

The yields of ketones reported by Nenitzescu and Ionescu were usually rather small. By agitating 2000 cc. of cyclohexane and 300 grams of acetyl chloride with 600 grams of anhydrous aluminum chloride for 36 hours, a relatively small quantity of 1-methyl-2-acetyl-cyclopentane, of boiling point 167°-168° C. at 759 mm. and d_4^{20} 0.8976, was obtained.

Nenitzescu and Ionescu also investigated the reaction of cyclohexane with chlorocyclohexane and other chloro-compounds. In the presence of anhydrous aluminum chloride a vigorous reaction took place, to yield a reaction product consisting of saturated hydrocarbons (not containing six-membered rings) as well as a sludge of aluminum chloride and unsaturated polymers of cyclohexane. It was believed that the saturated hydrocarbons of the formulas $C_{12}H_{22}$ and $C_{18}H_{32}$ were produced by reactions of the type

$$2C_6H_{12} \longrightarrow C_6H_{11}C_6H_{11} + 2H$$
$$3C_6H_{12} \longrightarrow C_6H_{11}C_6H_{10}C_6H_{11} + 4H\,,$$

the hydrogen, thus formed, reducing the chlorocyclohexane (or other chlorohydrocarbon present) which acts as a hydrogen acceptor.

The direct production of ketones from saturated hydrocarbons has been the subject of a number of industrial developments. Procedures are described by the I. G. Farbenindustrie A.-G.[101] for the synthesis of various ketones by treatment of paraffin or cycloparaffin hydrocarbons with acid chlorides, or with carbon monoxide under pressure, in the presence of a Friedel-Crafts condensing agent. The following examples are given of this process:

1. An autoclave is charged with 86 parts of a petroleum fraction, boiling between 60° and 70° C., together with 98 parts of phosgene and about 133 parts of aluminum chloride and heated to 100° C. A quantitative conversion into ketones of the polymethylene and paraffin series is said to take place.
2. Into a cool autoclave are charged 58 parts of n-butane and 85 parts of the double compound of phosgene and aluminum chloride, obtained by incorporating 5 parts of liquid phosgene with 2 parts of anhydrous aluminum chloride. The autoclave is then heated to 90° C. and kept at this temperature for 6 hours. After cooling, the pressure is released and the reaction products are separated in the usual manner. A yellow oil with an aromatic odor and which boils mainly between 120° and 150° C. at 15 mm. is obtained.
3. Seventy-eight parts of acetyl chloride and 100 parts of hexane (a slight excess above the quantity stoichiometrically required) are fed into an autoclave containing about 150 parts of anhydrous aluminum chloride. The mixture is heated for 2 hours at 100° C. The product obtained consists principally of ketones of the polymethylene series including octanone, for example.
4. One hundred parts of hexane are heated in an autoclave for 2 hours at 100° C. with 70 parts of benzoyl chloride and 66 parts of anhydrous aluminum chloride. The product of this reaction consists largely of ketones which boil between from 120° to 250° C. at 12 mm.
5. One hundred parts of cyclohexane are heated in an autoclave for 2 hours at about 100° C. with 66 parts of aluminum chloride and 39 parts of acetyl chloride. Ketones which boil between from 150° to 250° C. at atmospheric pressure are formed.

The manufacture of keto-acids by the reaction of petroleum fractions with dibasic organic acid anhydrides has been described by Bruson.[102] As an example of his procedure, 30 parts of phthalic anhydride and 100 parts of gasoline are made to react at 70° to 90° C. in the presence of 60 parts of aluminum chloride. After the evolution of hydrogen chloride ceases the hot product is treated with a solution of sodium carbonate, the unaffected gasoline is removed by distillation, and the precipitated aluminum hydroxide filtered out. An aqueous solution of the sodium salt of the keto-acid is thus obtained, from which the free acid may be precipitated by the addition of dilute sulphuric acid. The reaction between the petroleum hydrocarbons and phthalic anhydride may be represented by

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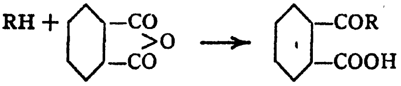
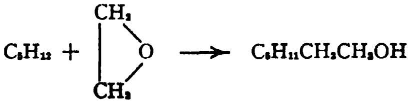
[101] British Patent 327,411, 1928; *Brit. Chem. Abs.* **B**, 1930, 602. Hopff, German Patent 517,718, 1927; *Chem. Abs.*, 1931, 25, 1258. German Patent 520,154, 1927; *Chem. Abs.*, 1931, 25, 3664; *cf.* Schaarschmidt, French Patent 735,786, 1931; *Chem. Abs.*, 1933, 27, 991. Holloway and Krase (*Ind. Eng. Chem.*, 1933, 25, 497) studied the reaction of benzene and carbon monoxide under pressure in the presence of aluminum chloride to yield benzaldehyde.

[102] U. S. Patent 1,882,762, Oct. 18, 1932; U. S. Patent 1,894,460, Jan. 17, 1933; *Chem. Abs.*, 1933, 27, 2458; U. S. Patent 1,896,608, Feb. 7, 1933; *Chem. Abs.*, 1933, 27, 2692; French Patent 703,490, 1930; *Chem. Abs.*, 1931, 25, 4282; British Patent 365,038, 1930; *Brit. Chem. Abs.* **B**, 1932, 494; all patents assigned to Resinous Products and Chemical Co.



The heavy-metal salts of such acids are insoluble in water but soluble in organic solvents such as toluene, turpentine, and linseed oil. The cobalt, manganese, and lead salts are stated to be effective driers for drying oils. The esters of these acids, particularly the ethyl, butyl and bornyl esters, are high-boiling viscous oils which may be used as either solvents or plasticizers for nitrocellulose.

According to the I. G. Farbenindustrie A.-G.,[103] alkylene oxides, such as ethylene oxide, may be condensed with paraffin, cycloparaffin, and benzenoid hydrocarbons in the presence of a Friedel-Crafts condensing agent (anhydrous aluminum chloride) to yield primary alcohols. Besides ethylene oxide, other alkylene oxides, such as 1,2- and 1,3-propylene oxides, isobutylene oxide and trimethylethylene oxide, may be used. Substances capable of forming such oxides during the reaction, as for example glycol chlorohydrins, may also be employed. Hydrocarbons, including pentane, hexane, heptane, dodecane, octadecane, cyclohexane, hexahydrotoluene, benzene, and aromatic hydrocarbons in general, and other condensing agents, such as boron fluoride and anhydrous ferric chloride, can be used. The process is exemplified by the direct condensation of n-pentane with ethylene oxide yielding *n-heptanol* according to the equation:



$$C_5H_{12} + \begin{array}{l} CH_2 \\ \;|\;\;\diagdown \\ \;|\quad\; O \\ \;|\;\;\diagup \\ CH_2 \end{array} \longrightarrow C_5H_{11}CH_2CH_2OH$$

This procedure appears to offer a method for the preparation of the higher straight chain primary aliphatic alcohols, some of which seem to present commercial possibilities in the manufacture of special soaps. Examples of the application of this condensation are the production of phenylethanol from benzene and ethylene oxide; n-heptanol, from n-pentane and ethylene oxide; a mixture of higher primary alcohols from kerosene and ethylene oxide; and of hydroxyethylcyclohexane from cyclohexane and ethylene oxide. Thus, condensation of 500 parts of n-pentane with ethylene oxide at room temperature in the presence of 250 parts of anhydrous aluminum bromide produced 25 parts of an oil, boiling range 160° to 190° C., containing considerable amounts of n-heptanol. Higher primary alcohols can be made from kerosene in the following manner:

One hundred fifty parts of anhydrous aluminum chloride are added to 500 parts of kerosene in an autoclave. This mixture is treated with ethylene oxide at room temperature and at about 1.5 atmospheres until there is no further decrease in pressure. The reaction product consists of a brownish colored, very viscous lower layer and a colorless upper layer. The latter contains only unchanged petroleum and is withdrawn. The lower layer is mixed with ice and the resulting 32 parts of oily product are separated from the water. The oil boils between 150° and 200° C. at 12 mm. and consists principally of higher alcohols.

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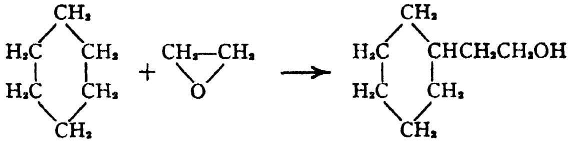
[103] British Patent 354,992, 1931; *Brit. Chem. Abs.* B, 1932, 12; see also Chapter 23.

The preparation of hydroxyethylcyclohexane is carried out by adding 50 parts of ethylene oxide, with cooling and agitation, to a mixture of 500 parts of cyclohexane and 132 parts of anhydrous aluminum chloride. The aluminum chloride is gradually converted into a viscous pasty mass. Unaltered cyclohexane is drawn off and the tough residue is decomposed with ice-water and steam-distilled, after the addition of 100 parts of concentrated hydrochloric acid. After extraction of the aqueous distillate with ether, the extract yields 70 parts of an oil boiling mainly between 95° and 105° C. at 13 mm., and consisting largely of hydroxyethylcyclohexane. Its formation may be represented thus:



hydroxyethylcyclohexane

Fohlen[104] described the condensation of paraffin hydrocarbons with phosgene to yield ketones or with phosgene and hydrogen to yield aldehydes. Various metals, metallic oxides, and salts are used as catalysts. The reactions believed to occur are exemplified by the following, representing the condensation of phosgene with methane and hydrogen:

$$2CH_4 + COCl_2 \longrightarrow CH_3COCH_3 + 2HCl$$

$$CH_4 + COCl_2 + H_2 \longrightarrow CH_3CHO + 2HCl$$

Trialkyl or triaryl borates have been suggested to replace the halogen derivatives generally used in the Friedel-Crafts reaction.[105] The reaction, for example, between tribenzyl borate and benzene to yield diphenylmethane may be represented by

$$(C_6H_5CH_2)_3BO_3 + 3C_6H_6 + AlCl_3 \longrightarrow 3C_6H_5CH_2C_6H_5 + 3HCl + AlBO_3$$

Miscellaneous Reactions of Paraffins and Cycloparaffins

According to Meigs,[106] *sulphur monochloride* reacts vigorously with unsaturated hydrocarbons, and at a slow rate with saturated hydrocarbons, the slow evolution of hydrogen chloride gas continuing with the latter for many hours. Subsequently, Lorand[107] examined the effect of sulphur monochloride on various saturated hydrocarbons and found that a reaction usually occurred. Various lubricating oils reacted violently with evolution of hydrogen chloride, higher kerosene fractions were attacked rather less vigorously, and various gasoline fractions changed color when mixed with this reagent, depositing a dark sediment on standing. A more energetic reaction occurred on heating. The branched chain diisoamyl was found to react energetically with sulphur monochloride at 100° C. After heating for six hours, during which time a slow evolution of hydrogen chloride took place, the color of the liquid became very dark and sulphur was deposited on cooling. Lorand believed that straight chain paraffin hydrocarbons are slowly chlorinated by sulphur monochloride. With branched chain paraffins this chlorination takes place somewhat more rapidly. On prolonged heating the chlorinated products lose hydrogen chloride and the resulting unsaturated substances are either chlorinated or polymerized. These reactions may be represented as follows:

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[104] French Patent 680,586, 1928; *Chem. Abs.*, 1930, **24**, 3799.

[105] Kaufmann, German Patent 555,403, 1930; *Chem. Abs.*, 1932, **26**, 5101.

[106] *Ind. Eng. Chem.*, 1917, **9**, 655.

[107] *Ind. Eng. Chem.*, 1927, **19**, 733.

$$(1)\ >CH{-}CH_2{-} + S_2Cl_2 \longrightarrow HCl + S_2 + >CH{-}CHCl{-}$$

$$(2)\ >CH{-}CHCl{-} \longrightarrow >C{=}CH{-} + HCl$$

Antimony chloride ($SbCl_5$) reacts with hydrocarbons containing a tertiary hydrogen atom (e.g., 2-methylpentane, methylcyclohexane) after a short period, whereas a primary or secondary linking (e.g., in such compounds as n-heptane, 2,2-dimethylbutane, cyclopentane or hexane) is attacked only at a higher temperature. Hydrogen chloride is liberated and the products are probably addition compounds, according to Schaarschmidt and Marder.[108] This behavior with antimony chloride can be used to detect the presence of compounds containing tertiary hydrogen linkages, though reaction of hydrocarbons containing primary and secondary hydrogen atoms is induced by the presence of the former.

When many saturated hydrocarbons are heated to temperatures above about 200° C. with *elemental sulphur,* a reaction occurs with the production of hydrogen sulphide, together with other substances. The action of sulphur on petroleum hydrocarbons is more fully discussed in Chapter 19. From the products of the action of elemental sulphur on methylcyclohexane at elevated temperatures Friedmann[109] isolated thiocresol, and Markownikow[110] similarly obtained xylene from an octonaphthene. Though some of the simple saturated hydrocarbons, such as cyclohexane, are stable with sulphur at temperatures of about 200° C., many of the higher paraffins and heavy petroleum greases are vigorously attacked under these conditions.[111]

Chlorosulphonic Acid, HSO_3Cl, is a sulphonating agent.[112] Marx and Brodersen[113] prepared sulphonic acids by the action of chlorosulphonic acid on petroleum hydrocarbons. Products made by sulphonating brown-coal tar oils or mixtures of petroleum hydrocarbons with aromatic or hydroaromatic hydrocarbons or their derivatives in this manner have been suggested as insecticides and fungicides.

Saturated hydrocarbons are attacked by a number of oxidizing agents. *Benzoyl peroxide* oxidizes some of the lower paraffins yielding mixtures in which aliphatic alcohols have been identified. By heating benzoyl peroxide with a purified petroleum fraction, boiling between 95° and 100° C., Böeseken and Gaster[114] observed the production of carbon dioxide, benzene, benzoic acid, heptylbenzene and, probably, a tertiary heptanol. n-Octane begins to react with benzoyl peroxide at 100° C., and carbon dioxide, benzene and benzoic acid are formed initially. What appeared to be a mixture of secondary octanols was obtained by hydrolysis of the neutral products of this reaction.

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[108] *Z. angew. Chem.*, 1933, **46**, 151; *Chem. Abs.*, 1933, **27**, 2418.

[109] *Petroleum*, 1916, **11**, 978; *Chem. Soc. Abs.*, 1917, **112** (1), 13.

[110] Markownikow and Spady, *Ber.*, 1887, **20**, 1850.

[111] Prothiere, *Pharm. Ztg.*, 1903, **48**, 78: *Chem. Zentr.*, 1903, 1, 492.

[112] For the action of chlorosulphonic acids on diisopropyl and isopentane see Aschan, *Ber.*, 1898, **31**, 1801. These reactions have already been mentioned in Chapter 46.

[113] German Patent 551,199, 1927; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, **26**, 4408.

[114] *Rec. trav. chim.*, 1930, **49**, 102; *Brit. Chem. Abs.* **A**, 1930, 316.

Chapter 48

Occurrence, Properties and Uses of Naphthenic Acid

The naphthenic acids are carboxylic acids which are obtained from various crude petroleums or their distillates. The name is derived from the circumstance that they were first discovered in naphthene- (cycloparaffin-) containing crude oils from Russia and Rumania. The name naphthenic acids is also expressive of the chemical relationship of these acids with the naphthene hydrocarbons, a similarity which later work has fully substantiated.

The naphthenic acids probably occur to some extent in most petroleums but they are usually associated with those of Rumania, South Russia and the Caucasus. Great differences exist, however, between the naphthenic acid contents and the chemical characteristics of these acids from various crudes. Whereas, for example, Russian petroleums often contain quantities of relatively simple low-boiling naphthenic acids having a very persistent and somewhat disagreeable odor, the Gulf Coast (U.S.A.) petroleums contain higher-boiling acids which are practically odorless and can be salted out of their aqueous solutions readily.

The actual content[1] of naphthenic acids in various crudes, and distillates derived therefrom, has been very little investigated and little information is available on it. The crude acids obtained by alkali treatment of oils often contain considerable amounts of other substances, including dissolved hydrocarbons, phenols, and sulphonated products (if the oil has been previously acid-treated). According to some investigators the Rumanian crudes possess the highest content of naphthenic acids and the Russian and Galician oils rank somewhat lower in this respect. Naphthali[1a] gave figures for the naphthenic acid content of several oils ranging from 0.07 per cent to 2.4 per cent.

According to Lidow,[2] the naphthenic acid content of Russian crude and masout is 0.83 to 1.3 per cent. Schulz[3] obtained naphthenic acids from unrefined Galician distillates in yields corresponding to 0.05 to 0.84 per cent of the distillate. Krämer and Böttcher[4] examined a German petroleum from Oelheim and an Alsatian petroleum and found naphthenic acids (as well as small amounts of phenols) to the extent of 0.081 per cent and 0.136 per cent, respectively. A Russian crude from Balachani-Sabunchi examined by Goldberg and Gurvich[5] contained 1.06 per cent of naphthenic acids (average acid number 202 and average molecular weight 277), which were monobasic. The acidity and naphthenic acid content of the various distillates of this crude increased with rising boiling point and decreased at the upper end, the maximum being the distillate of 0.882. According to Vuistavkina[6] crude Emba (Russian) petroleum contains 0.43 to 0.74 per cent of naphthenic acids, while the distillates contain 0.18 to 1.44 per cent of these acids having molecular weights which vary from 218 to 466. The refining of a gas-oil distillate of a Japanese petroleum yielded about 0.14 per cent of crude petroleum acids, of which 7.7 per cent consisted of higher fatty acids.[7] Holzmann and von Pilat[7a] established the presence of myristic, palmitic, stearic, and arachidic acids in a spindle oil extract.

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[1] For method for analysis of naphthenic acids see Malyatski, *Azerb. Neft. Khoz.*, 1932, No. 10, 87; *Brit. Chem. Abs.* **B**, 1933, 292; Virabyantz and Artemiev, *Groznenskii Neftyanik*, 1930-31, 1. No. 2-3; Suppl. No. 1, Sci. Sect. 9-31; *Chem. Abs.*, 1931. **25**. 3472.

[1a] "Chemie, Technologie und Analyse der Naphthensäuren," Wissenschaftliche Verlagsgesellschaft m.b.H.. Stuttgart, 1927.

[2] *Führer durch die Fettindustrie,* 1905, 107; *Seifensiederzeitung,* 1905, **32**, 834; *Chem. Zentr.*, 1905, **2**, 1610.

[3] *Chem.-Ztg.*, 1908, **32**, 596; *Chem. Abs.*, 1908, **2**, 2735. This investigator also reported that the acidity of distillates increased on standing due to oxidation. Muishkin (*Grozneski Neft.*, 1930-1931, 1, **2**, 44; *Brit. Chem. Abs.* **B**, 1931, 1035) reports values of 0.012 to 1.94 per cent for various crude distillates.

[4] *Ber.*, 1888, **20**, 596.

[5] *Azerb. Neft. Khoz.*, 1928. **5**, 46; *Chem. Abs.*, 1928, **22**. 3767.

Malyatskii and Margolis[7b] determined the solubility, acid number, molecular weight, and dissociation constant of naphthenic acids from naphtha, kerosene, and gas-oil fractions of Baku crude. Solubilities in water of the acids from the three fractions were 37, 22 and 7 milligrams per liter, respectively. Acid numbers were 316.5, 259.9 and 195.2; molecular weights, 176.8, 216, 287; and dissociation constants, 8.84×10^{-7}, 8.21×10^{-7}, 6.02×10^{-7}, respectively.

The Russian crudes apparently contain approximately 1 per cent of naphthenic acids but in the majority of crudes from other parts of the world the naphthenic acid content is much less, usually not more than 0.1 per cent. Naphthali[7c] gives the figures in Table 157 for the naphthenic acid content of some American crudes:

TABLE 157.—*Naphthenic Acid Content of American Crude Oils.*

Source	Naphthenic Acid Content Approximate Per Cent
Winkler County (Texas)	0.30
Howard County (Texas)	0.07
Runnels County (Texas)	0.03
Hosston (Louisiana)	0.70
Saginaw (Michigan)	0.03
Smackover (Arkansas)	0.03
Midcontinent (Pipe Line)	0.04
Midcontinent	0.03
Pennsylvania	0.03
Gulf Coast Crude	0.60
Distillate from Gulf Coast Crude (Viscosity, 300 sec.)	1.24
Distillate from Venezuela Crude (Viscosity, 500 sec.)	1.00
California (Southern California and San Joaquin Valley Crude)	0.1 to 3.0
Gillies Siding (Canada)	0.07
Bothwell (Canada)	0.16 to 0.46
Petrolia (Canada)	0.11

As regards the actual mode of formation of naphthenic acids from petroleum several theories have been put forward[8] but a number of facts appear to indicate that a large proportion, if not the whole, of the naphthenic acids obtained are actually produced by oxidation of certain readily oxidized cycloparaffins during the alkali wash of refining operations or during distillation.[9] As early as 1884,

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[6] *Neft. Khoz.*, 1930, **18**, 1000; *Brit. Chem. Abs.* **B**, 1931, 283.

[7] Tanaka and Kuwata, *J. Fac. Eng. Tokyo Imp. Univ.*, 1928, **17**, 293; *Brit. Chem. Abs.* **B**, 1929, 117.

[7a] *Brennstoff-Chem.*, 1931, **12**, 41; *Brit. Chem. Abs.* **B**, 1931, 327; *Brennstoff-Chem.*, 1933, **14**, 263; *Brit. Chem. Abs.* **B**, 1933, 772; *J. Inst. Pet. Tech.*, 1933, **19**, 414A.

[7b] *Azerb. Neft. Khoz.*, 1933, No. 3, 75; *Chem. Abs.*, 1933, **27**, 4153.

[7c] *Fettchem. Umschau*, 1933, **40**, 149; *Chem. Abs.*, 1933, **27**, 5062.

[8] For a review of these theories see Tiutiunnikov, *Neft. Khoz.*, 1926, **10**, 797; *Brit. Chem. Abs.* **B**, 1928, 114. See also Petrov and Ivanov, *J. A. C. S.*, 1932, **54**, 239.

[9] von Braun, *Ann.*, 1931, **490**, 100; *Chem. Abs.*, 1932, **26**, 2306. The soluble portion of sulphur dioxide extract of California kerosene, treated with alkali in the presence of air, gives naphthenic acids (A) which are only *poorly soluble* in sulphur dioxide. From the insoluble portion, or raffinate of the kerosene, treatment with alkali and air gives naphthenic acids (B) which are *very soluble*

Schaal[10] proposed oxidation of petroleum fractions by air in alkaline solution at high temperatures as a method of producing acid oxidation products. It was shown, moreover, by Charitschkoff[11] that oxidation of naphthene hydrocarbons, either photochemically or by the method of Schaal, resulted in the formation of monocarboxylic naphthenic acids as well as considerable amounts of polynaphthenic acids. The latter substances were viscous tribasic pseudo-acids, which are probably bicyclic condensation products of the naphthenic acids. The view that naphthenic acids are formed by alkaline oxidation of cycloparaffin hydrocarbons is fast gaining support, notably as a result of the important researches of von Braun, Petrow and others and opens up a wide field of practical possibilities in the direction of increasing the quantities of acids obtainable from petroleum fractions.

Pyhälä[11a] reported that distillates from a Russian petroleum contained 12 times as much naphthenic acids as the original oil, and a Rumanian oil gave a similar result. He believes, however, that the acids exist in the crude as an unsaponifiable complex. This view was supported by experiments in which the acid treatment of the crude was varied, resulting in a change in the content of naphthenic acids found in the distillate.

EXTRACTION OF NAPHTHENIC ACIDS FROM PETROLEUM

Naphthenic acids may be extracted from crude oils or distillates by the use of aqueous sodium hydroxide solutions in which the acids dissolve yielding sodium naphthenates.[12] In the acid refining of many petroleum distillates, however, the oil is first treated with a certain amount (which varies with the distillates to be treated) of concentrated sulphuric acid to remove asphaltic materials or sulphur compounds. The oil is then subjected to a dilute alkali wash to remove the last traces of acids and sulphonated products. The lyes from the latter treatment on acidification yield considerable amounts of free naphthenic acids.[13] The raw acids often contain considerable proportions of impurities such as hydrocarbons. The presence of these neutral hydrocarbons in the lye is to be ascribed to the difficulty of separating the aqueous lye from the main oil bulk on account of the high emulsifying character of the sodium naphthenates. The large-scale production of naphthenic acids free from neutral oils is for this reason rendered very difficult and the last traces of hydrocarbons can usually only be removed by special treatments.

It has been contended[14] that the concentrated sulphuric acid of the acid wash actually condenses with the naphthenic acids to yield sulphonic acids of the type

$$\begin{array}{l}\mathrm{R.SO_3H}\\ |\\ \mathrm{COOH}\end{array}$$

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in sulphur dioxide. The high solubility of the (B) acids obtained from the initially insoluble raffinate clearly shows that naphthenic acids have been formed during the alkali treat. (Private communication from von Braun.)

[10] German Patent 32,705, 1884; British Patent 12,806, 1884; *J.S.C.I.*, 1885, 4, 679.

[11] *Neft. Djelo*, 1912, 10, 14; *Chem. Ztg.*, 1912, 36, 530; *Chem. Abs.*, 1913, 7, 2465. *J. Russ. Phys.-Chem. Soc.*, 1908, 40, 1757; *Chem. Zentr.*, 1909, 1, 854; *Petroleum*, 1909, 5, 316; *Chem. Zentr.*, 1910, 1, 1199.

[11a] *Chem. Ztg.*, 1933, 57, 273, 294; *Brit. Chem. Abs.* B, 1933, 452; *Chem. Abs.*, 1933, 27, 4912.

[12] See, for example, Vuiborova, *Aserb. Neft. Khos.*, 1932, 7, 79; *Chem. Abs.*, 1932, 26, 5740. Novikov-Vakulenko, *Aserb. Neft. Khos.*, 1932, 11, 58; *Chem. Abs.*, 1933, 27, 1492.

[13] Lemmon, U. S. Patent 1,823,614, Sept. 15, 1931; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, 26, 295.

[14] Pyhälä, *Petroleum*, 1908, 3, 1313; *J.S.C.I.*, 1908, 27, 1054. See also, Vuishetravskii, *Neft. Khos.*, 1932, 22, 241; *Chem. Abs.*, 1932, 26, 4450.

which are thus extracted with the naphthenic acids during the alkali wash. However, Gurwitsch[15] found that the crude naphthenic acids extracted from a kerosene fraction by direct alkali treatment did not differ in chemical and physical properties from the acids extracted from the same distillate previously subjected to an acid refining. It is probable, however, that the acids present in the higher fractions of petroleums more readily undergo sulphonation during acid refining. Tanaka and Nagai[16] have also shown that the properties of the naphthenic acids obtained directly from a Japanese petroleum distillate without previous treatment with sulphuric acid were practically identical with those of the naphthenic acids from the waste lyes produced in the ordinary alkali refining of the same distillate after acid refining.

The production of naphthenic acids as a by-product of the acid refining of distillates was developed on a considerable scale in Russia before the War, notably by the firm of Nobel Bros. Many of the American petroleums are probably too poor in acid constituents to serve as a commercial source of these materials but the crudes of Galicia and Rumania have been utilized. The initial stage in the refining of many distillates consists in treatment with concentrated sulphuric acid, the quantity of acid used being somewhat variable but usually 0.5 to 1.0 per cent for benzines, 2 to 4 per cent for kerosenes, and 5 to 10 per cent for lubricants. The acid layer is then run into water to yield the well-known "acid-tar," a fruitful but almost untapped source of sulphonated products. The acid-treated oil is then washed with a dilute aqueous solution of sodium hydroxide, the whole mass being kept well agitated with a current of air or steam. From a technical point of view the separation of this dilute alkaline solution from the treated oil often presents considerable difficulties, since, as mentioned previously, very stable emulsions of the oil-in-water type are frequently formed. Methods of dealing with these emulsions vary with the characteristics of the oil under treatment.

From the dilute caustic solution used in the alkaline treatment of oils, the naphthenic acids may be obtained in the free state by acidifying with sulphuric acid. If instead of sulphuric acid, sulphur dioxide is used for this purpose the resulting sodium sulphite may be causticized with lime and sodium hydroxide is recovered.[17]

If the particular distillate does not need acid refining, or if other refining methods are more suitable, the naphthenic acid constituents may be removed by an alkali-wash without any preliminary treatment. There is an increasing tendency to displace the acid treatment in favor of refining methods depending upon the use of adsorbent earths, which can be easily revivified by roasting and used several times. An apparatus for the direct extraction of naphthenic acids from oils without preliminary acid treatment has been described by Emmuil.[18] This consists of a vertical cylinder the middle section of which is provided with a steam coil to heat the gas oil or other distillates under treatment, to 70°-75° C. The oil enters at the bottom through a perforated pipe and leaves at the top. The causic soda solution is introduced at the top of the cylinder counter-current to the oil and is discharged at the bottom together with the soap formed.

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[15] Gurwitsch-Moore, "The Scientific Principles of Petroleum Technology," D. Van Nostrand Co., New York, 1932, 127.

[16] *J. Fac. Eng. Tokyo Imp. Univ.*, 1926, **16**, 183; *Chem. Abs.*, 1926, **20**, 2832.

[17] Gurwitsch, *Brennstoff-Chem.*, 1925, **6**, 322; *Chem. Abs.*, 1926, **20**, 660.

[18] *Aserb. Neft. Khoz.*, 1930, No. 11, 90; *Chem. Abs.*, 1931, **25**, 1066. See also Atal'yan and Zlatkin, *Aserb. Neft. Khoz.*, 1931, No. 2-3, 64; *Chem. Abs.*, 1931, **25**, 3815. *Cf.* Wheeler and Prutzman, U. S. Patent 1,784,262, Dec. 9, 1930; *Brit. Chem. Abs.* **B**, 1931, 795.

A typical process for the production of saponifiable products from mineral oils is that of Maitland,[19] which is conducted in the following manner: Twenty-three hundred barrels of lubricating stock are thoroughly agitated with about 75 barrels of 93.5 per cent sulphuric acid and then allowed to settle. Three distinct layers are formed, namely a top layer, "A," consisting of 2175 barrels of lubricating stock with approximately 0.75 per cent sulphuric acid in suspension; a middle layer, "B," composed of 180 barrels of a mixture of sludge and acid; and finally a bottom layer, "C," consisting mainly of acid with some dissolved sludge. These layers are separated and layer "A" is slowly agitated with about 300 barrels of dilute sodium hydroxide solution and permitted to settle. Two layers are formed, namely a top layer, "D," composed chiefly of lubricating stock amounting to about 1925 barrels, and 550 barrels of a bottom layer, "E," which is a mixture of lubricating oil, soap (alkali naphthenates), and alkaline salt solution. This lower layer is drawn off, agitated with about 150 barrels of 7 per cent sulphuric acid at 100° C. and then 150 barrels of hot water are added. On settling the mixture separates into two layers, the upper layer, "F," consisting of approximately 250 barrels of saponifiable acids admixed with some mineral oil, while the bottom layer, "G," is the salt water resulting from the decomposition of the soap. After drawing off this bottom layer, layer "F" may be saponified with a hot solution of about 51 Bé. caustic soda to yield a bright soap containing very little water. If sufficient care is taken to allow the product "E" to settle properly it will separate into three layers, namely a top layer "H" (18 per cent of total) containing mainly mineral oil, a middle layer "I" (39 per cent) containing the soap, and a bottom layer "J" (43 per cent) of alkali salts and water. The soaps obtained in this process are said to be applicable to all purposes for which soaps from animal or vegetable oils are adapted. Maitland also suggests that the acid sludge layer "B" may be worked up to give a soap which is similar to the product obtained by the alkali wash treatment and contains only about 0.4 per cent of sulphur. This soap is made by mechanical mastication of the sludge with warm water until the acid content has been reduced to below 2 per cent. The residual compounds settling to the bottom of the digester are saponifiable oils containing some dissolved and suspended matter.

As the alkali salts of the naphthenic acids are useful materials, the acids are usually worked up in this form. Partial concentration of ordinary alkali sludge can be effected and it is generally necessary to salt out the soaps from the concentrated solution. A plant for the separation of naphthenic acids from a kerosene alkali sludge was described by Shiperovich and Gurwitsch.[20] The sludge, containing about 10 to 25 per cent of naphthenic acids, is atomized with hot gases and concentrated to about 40 per cent naphthenic acids, which are then salted out. According to Stock[21] petroleum soaps are obtained by acidifying alkali sludge with sufficient sulphuric acid to separate a very small quantity of free naphthenic acids, after which the remaining soaps may be salted out of solution.

The direct production of naphthenic acid soaps by redistilling lubricating stocks (containing naphthenic acids) in the presence of caustic soda, or other alkalies, was described by Coleman and Hughes.[22] The hot distillation residues are discharged into water and the oil which separates from the aqueous metal naphthenates is taken off in stages.

Andrews and Lauer[23] extracted the alkaline residue, obtained from the distillation of naphthenic-base crudes, with 80 to 95 per cent alcohol. Separation and distillation of the alcohol yields the sodium soaps from which the naphthenic acids are recovered.

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[19] U. S. Patents 1,425,882 and 1,425,883, Aug. 15, 1922; *Chem. Abs.*, 1922, **16**, 3388; U. S. Patents 1,425,884 and 1,425,885, Aug. 15, 1922; *Chem. Abs.*, 1922, 16, 3388; all patents assigned to Sun Oil Co.

[20] *Neft. Khoz.*, 1928, No. 12, 26; *Brit. Chem. Abs.* **B**, 1929, 585; *Chem. Abs.*, 1929, **23**, 1500.

[21] Russian Patent 46,666, 1929; *Chem. Abs.*, 1931, **25**, 1067.

[22] U. S. Patent 1,676,687, July 10, 1928; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1928, **22**, 3290. Humble Oil and Refining Co., British Patent 304,926, 1928; *Brit. Chem. Abs.* **B**, 1929, 274. Mild oxidation of lubricating distillates in the presence of alkalies is also suggested by Coleman: U. S. Patent 1,886,647, Nov. 8, 1932; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 1497.

[23] U. S. Patent 1,804,451, May 12, 1931; assigned to Texas Co.; *Brit. Chem. Abs.* **B**, 1932, 92.

Rogers[24] suggested removing naphthenic acids from hydrocarbon oils by vaporizing the oil and passing the vapors upward through a tower, in the lower part of which molten caustic soda is present. A small amount of reflux is maintained in the upper part of the tower to prevent entrainment of sodium compounds. The residues may be treated with concentrated sulphuric acid to liberate the naphthenic acids and recover the contained oil.[25]

PURIFICATION OF CRUDE NAPHTHENIC ACIDS

The crude naphthenic acid soaps recovered from alkali sludge yield, on acidification, a mixture of naphthenic acids and other substances. The impurities present in the acids, or their soaps, are primarily neutral hydrocarbons which, on account of the high emulsifying properties of the naphthenic acids and their salts, are exceedingly difficult to remove. Besides hydrocarbons, petroleum resins and asphaltic materials are often present. However, from a technical standpoint the problem of removing neutral hydrocarbons from naphthenic acids is of primary importance.

Several methods of removing neutral hydrocarbon oils have been proposed. Redistillation of the crude naphthenic acids is hardly effective, since it has been shown that distillation of oils containing naphthenic acids carry over acids boiling up to 50° C. above the range of the respective petroleum cuts, the same effect being observed with steam or vacuum distillation.[26] According to Bauer,[27] crude naphthenic acids may be freed from neutral oils by stirring them with aniline or o-toluidine. After standing for some time the lower layer is separated and the solvent is distilled off. Naphthenic acids of 98-99 per cent purity remain in the still and a repetition of the process results in the production of acids almost completely free from mineral oils. The crude acids can be refined by extracting, with petroleum ether, a solution of them in alcohol containing 30 per cent sodium hydroxide and then distilling the alcohol. The residue is treated with dilute sulphuric acid, dissolved in petroleum ether, washed, dried over anhydrous sodium sulphate and phosphorus pentoxide, and distilled under a pressure of 3 mm.[28]

Alleman[29] developed a process for separating the mineral oil and petroleum resins in alkali sludge from lubricating distillates. The original alkali sludge, or soap emulsion, had the following typical composition:

	Per Cent
Soap (sodium salts)	11.6
Petroleum resins	17.1
Mineral lubricating oil	46.
Sodium sulphate	2.3
Water	23.

If this soap, oil and water emulsion is treated with gasoline, practically no separation takes place because of the presence of positively charged particles or droplets. Small amounts of certain salts of lithium, sodium, or potassium added to the emulsion in gasoline effect an immediate separation. In practice the purification consists in dissolving the soap emulsion in hot gasoline and then adding

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[24] Canadian Patent 309,100, 1931; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1931, **25**, 1984.

[25] Deutsche Gasolin A.-G., British Patent 360,277. 1931; *Chem. Abs.*, 1933, **27**, 594.

[26] Gutt, Joanesyan and Novruskhanov, *Azerb. Neft. Khoz.*, 1930, No. 9, 138; *Chem. Abs.*, 1931, **25**, 586.

[27] German Patent 302,210. 1916; *J.S.C.I.*, 1918, **37**, 330A.

[28] Smirnov and Buks, *Azerb. Neft. Khoz.*, 1932, **11**, 60; *Chem. Abs.*, 1933, **27**, 1492.

[29] U. S. Patent 1,694,461, Dec. 11, 1928; assigned to Sun Oil Company; *Chem. Abs.*, 1929, **23**, 696.

10 per cent of a concentrated aqueous solution of common salt. On allowing to stand, separation takes place and the top gasoline layer (containing the mineral lubricating oil originally held by the emulsion) is drawn off. After three such extractions with gasoline and salting out with sodium chloride solution, the soap solution is substantially free from mineral oils but still contains some petroleum resins. On evaporating this purified soap solution, and cooling to 5° C. or below, the soaps may be separated leaving the sodium sulphate in solution. On decomposing these soaps with mineral acids, the free organic acids are obtained with an acid number of about 103.5, as contrasted with the value of 30 for the crude acids before treatment.

Another procedure of Alleman[80] deals with the purification of alkali sludges, similar to those just described. The sludge is introduced into a closed upright boiler, water is added until it is approximately 58 per cent of the whole mixture, and the mass is then heated to a steam pressure of 60 pounds for 2 hours. Cooling is allowed to take place in the presence of compressed air (also at a pressure of 60 pounds) to prevent agitation of the liquid which otherwise would occur because of boiling as the pressure became less during the cooling step. A permanent separation is said to result, the top layer consisting of mineral oil and the bottom, a water layer containing soap, resin, and sodium sulphate. Soap is obtained by evaporating the lower aqueous layer and cooling the concentrated solution.

Coleman[81] described a process consisting essentially in a vacuum distillation of the mixture of oil and acids. Heavy fractions of, for example, Gulf Coast petroleum are washed with hot sodium hydroxide solution to remove acids as sodium salts. Addition of sulphuric acid to the aqueous alkaline wash precipitates the oily acids, which are again converted into their sodium salts. The sodium salts are dried, fluxed with 2 volumes of gas oil (boiling range, 250° to 350° C.) and the mixture is then heated rapidly to 510° F. and flashed into a vessel maintained under a vacuum of 1.5 mm. of mercury. The oil-free residue of naphthenates is run into water and naphthenic acids are recovered by acidification.

Bransky[82] proposed a method of separating naphthenic acids from lubricant distillates, e.g., from Louisiana crude, which involves treating the distillate with sufficient soda ash solution to neutralize the oil. The neutralized oil is then extracted with 10 to 20 per cent of methanol, ethanol, or isopropanol. The alcoholic extract is separated and distilled, and the alkali naphthenates remaining in the residue are purified by acidification and steam distillation. The viscous oily acid product yields a sodium salt which can be used as a detergent and a green copper salt applicable in naphtha solution as a wood preservative.

It will be seen from the foregoing that the purification of naphthenates (usually alkali salts), or free naphthenic acids, from dissolved or emulsified mineral oils can usually be effected by such processes as alkaline distillation, extraction of alkali salts with solvents, or extraction of adherent mineral oils from aqueous solutions of naphthenates by means of gasoline in the presence of emulsion-precipitating salt solutions.

The free naphthenic acids of Russian, Galician and Central European origin are frequently low-boiling liquids of very offensive odor, and in order to utilize such acids in the manufacture of detergents it becomes necessary to minimize this disagreeable odor. On the other hand, the naphthenic acids derived from American crudes, especially those of the lubricant distillates, are higher boiling, possess higher molecular weights, and are often without odor. For the deodorization of naphthenic acids of the Russian type, chemical treatment is usually necessary. Breda [33] recommended oxidizing agents, such as potassium permanganate, followed by distillation with superheated steam. It is stated that the objectionable odor of some naphthenic acids may be destroyed by the use of agents such as nitrous acid or hypochlorous acid, or their salts.[34] Pohl [35] suggested treating naphthenic acids, or their soaps, successively with reducing and oxidizing agents. Naphthenic acid soaps are also said to be deodorized by treatment with about ½ per cent of the alkali salts,of the peracids (percarbonate, persulphate or perborate), or with sodium peroxide.[36] Heating the soap solutions to 200° C. or higher in an autoclave has been advocated as a method of purification.[37]

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[80] U. S. Patents 1,694,462 and 1,694,463, Dec. 11, 1928; assigned to Sun Oil Co.; *Chem. Abs.*, 1929, **23**, 697.

[81] U. S. Patent 1,720,821, July 16, 1929; *Chem. Abs.*, 1929, **23**, 4230; British Patent 294,892; 1928; *Chem. Abs.*, 1929, **23**, 2030. Both patents assigned to Standard Oil Development Co.; *cf.* Becker and Sloane, U. S. Patent 1,785,242, Dec. 16, 1930; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 961.

[82] U. S. Patent 1,681,657, Aug. 21, 1928; *Chem. Abs.*, 1928, **22**, 3985; Canadian Patent 280,795, 1928; *Chem. Abs.*, 1928, **22**, 3041; both patents assigned to Standard Oil Co. of Indiana. Also British Patent 323,784, 1928; *Brit. Chem. Abs.* **B**, 1930, 313.

Schmitz [38] noted that hexa- and hepta-naphthenic acids which had been prepared synthetically had an odor similar to that of petroleum naphthenic acids. The odor of the petroleum acids was reduced by treatment with dilute aqueous sodium carbonate solution. The oxygen compounds in the acids, which were apparently phenols, were insoluble in sodium carbonate but soluble in potassium hydroxide solution, and had a dark color and an intense penetrating odor. Hydrogenation did not affect the odor of the crude acids but treatment with ozonized air for 1½ to 2 hours at 14° to 17° C. caused a slight reduction in the odor.

Crude naphthenic acids or their salts frequently possess a deep color which is undesirable in many respects. Various adsorbent materials, such as the hydrosilicate, tonsil, are said to effect decolorization. According to Gurwitsch,[39] naphthenic acids can be improved in color and odor by treatment with concentrated or fuming sulphuric acid. On the addition of a regulated amount of water, the sulphuric acid separates as a moderately mobile tar. Schrauth [40] described a method of making, from crude naphthenic acids, products of bright yellow color and having a better odor and higher acid value than the original acids. The crude naphthenic acids are condensed with formaldehyde or substances yielding formaldehyde, if necessary at elevated temperatures and pressures with or without the addition of condensing agents. Another procedure for the removal of impurities consists in the precipitation of naphthenic acids (either in the form of the acids themselves or as their salts) from aqueous solutions by.the addition of a volatile electrolyte (hydrogen chloride, acetic or nitric acid, or ammonia). The impurities are said to remain in solution.[41] Schmitz [42] noted that ozone at 50° C. bleached the acids slightly, a yellow precipitate being formed at the same time. At 100° C. the ozone caused a polymerization, the color of the acids changing to a wine-red.

Distillation under reduced pressure of Russian-type naphthenic acids minimizes both the odor and the dark color,[43] but it is doubtful if this treatment alone is sufficient.

[33] British Patent 19,477, 1906; *J.S.C.I.*, 1907, **26**, 464.
[34] Erdölverwertungsgesellschaft, German Patent 305,771, 1916; *J.S.C.I.*, 1918, **37**, 457A.
[35] German Patent 408,663, 1922; assigned to Jäger G.m.b.H.; *J.S.C.I.*, 1925, **44**, 459B.
[36] Vereinigte Chem. Werke, German Patent 200,684, 1906; *Chem. Abs.*, 1908, **2**, 3164.
[37] Stiepel, German Patent 305,702, 1916; *J.S.C.I.*, 1918, **37**, 476A.
[38] *Mat. grasses*, 1914, **7**, 4115; *J.S.C.I.*, 1914, **33**, 684; *Chem. Abs.*, 1914, **8**, 3360.
[39] *Brennstoff-Chem.*, 1925, **6**, 322; *Chem. Abs.*, 1926, **20**, 660.
[40] German Patent 390,847, 1920; *J.S.C.I.*, 1924, **43**, 460B.
[41] Bataafsche Petroleum Maatschappij, British Patent 300,264, 1927; *Chem. Abs.*, 1929, **23**, 3479.
[42] *Loc. cit.*
[43] Charitschkow, *J. Russ. Phys.-Chem. Soc.*, 1897, **29**, 691; *Chem. Soc. Abs.*, 1899, **76** (1), 42.

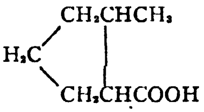
CONSTITUTION AND CHEMICAL PROPERTIES OF INDIVIDUAL NAPHTHENIC ACIDS

The separation of individual chemical substances from the complex mixture of acids obtained from petroleum is a problem of great difficulty and it is not surprising to find that many of the statements concerning them are often contradictory and the physical constants of the isolated acids, presumably chemical individuals, frequently widely divergent. The difficulty of isolating pure naphthenic acid individuals increases as the boiling point and molecular complexity increases, owing to the possibilities of isomerism and the probable occurrence of acids of different series. Heretofore our knowledge of the constitution of individual naphthenic acids was in a chaotic condition but the work of von Braun has shed much new light on the subject and has revealed a number of fundamental errors in the older conceptions. It is both convenient and instructive to discuss the gradual progress of fundamental chemical research on the naphthenic acids from a purely historical standpoint.

As mentioned, separation of individual naphthenic acids by straight distillation of the mixed acids is a matter of great difficulty and the problem has usually been attacked by first converting the free acids into derivatives which can be subjected to fractional distillation with less possibility of decomposition. For this purpose the esters, especially the methyl esters, have been most frequently employed. The esterification of naphthenic acids by an alcohol, such as methanol, can be effected by heating the mixture of acids and alcohol in the presence of about 3 per cent of dry hydrogen chloride or a small quantity of concentrated sulphuric acid.[44]

Eichler[45] was one of the first workers to employ esterification in the separation of the oily acids of Sarachany (Caucasian) petroleum, from which he extracted twelve different acids. Hell and Medinger[46] fractionated the ethyl esters of naphthenic acids extracted from a Rumanian crude and obtained what was considered to be an individual ethyl ester, boiling at 236° to 240° C. and having the formula $C_{11}H_{19}O_2C_2H_5$. Saponification of this ester yielded a naphthenic acid of the formula $C_{11}H_{20}O_2$, boiling at 258° to 261° C.

A great impetus to the chemical investigation of naphthenic acids was supplied by the work of Markownikow and Oglobin[47] on the saturated hydrocarbons of Russian naphtha. Markownikow[48] fractionated the methyl esters of Russian naphthenic acids and isolated several individual acids. Aschan[49] also isolated the same acids by a similar process of fractionation. It was shown by Markownikow[50] that the fraction of the methyl esters distilling at 160° to 165° C. consisted essentially of the compound $C_7H_{11}O_2CH_3$ which on hydrolysis yielded the heptanaphthenic acid, $C_7H_{11}COOH$, boiling at 213° to 214° C. This acid was assumed to be a stereoisomer of 1-methylcyclopentane-2-carboxylic acid,



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[44] Aschan, *Ber.*, 1890, **23**, 867; 1891, **24**, 2719; 1892, **25**, 886, 3661.

[45] *Bull. soc. nat. de Moscou*, **46**, 274; see Aschan, "Alicyclische Verbindungen," **1905**, 101; Budowski, "Die Naphthensäuren," J. Springer, Berlin, **1922**.

[46] *Ber.*, 1874, **7**, 1216; 1877, **10**, 455.

[47] *Ber.*, 1883, **16**, 1878.

[48] *Ann.*, 1899, **307**, 369.

[49] *Ber.*, 1899, **32**, 1766; *Chem. Soc. Abs.*, 1899, **76**, 672; *cf.* Markownikow, *Ann.*, 1899, **307**, 369; *Chem. Soc. Abs.*, 1899, **76**, 800.

[50] *Ber.*, 1892, **25**, 3361; *cf.* Aschan, *Ber.*, 1890, **23**, 867.

as the synthetic acid prepared by Coleman and Perkin[51] boiled at 219.5° to 220.5° C. The octanaphthenic acid, boiling point 237° to 239° C., of the formula $C_7H_{13}COOH$, was isolated by both Markownikow and Aschan. The latter worker also succeeded in isolating a number of the higher members among which may be mentioned a monanaphthenic acid, boiling point 251° to 253° C., and a decanaphthenic acid, boiling point 260° to 264° C. The research of these and other workers therefore showed that the naphthenic acids present in a number of crude petroleums, mostly of Russian or Rumanian origin, could be resolved, e g., by fractionation of their methyl esters, into a whole series of monobasic carboxylic acids of the general formula $C_nH_{2n-2}O_2$ with strong presumptive evidence of the existence therein of a polymethylene ring. The probable absence of hexahydrobenzoic acid (cyclohexane carboxylic acid) was indicated by the work of Aschan, and this fact, coupled with the results of Markownikow, further indicated that the essential basis of the naphthenic acid molecule is a cyclopentane ring.

Following the work of Aschan and Markownikow a number of investigators concentrated on the isolation of individual acids from the naphthenic acids derived from various petroleum oils or their distillates, though their efforts contributed little to our knowledge of the constitution of these substances. Thus, Krämer and Böttcher[52] converted the naphthenic acids of Alsatian petroleum into their methyl esters and subjected the latter to fractionation. Methyl esters corresponding to the two monobasic acids $C_{15}H_{28}O_2$ and $C_{18}H_{24}O_2$ were obtained. The former acid had d_4^{15} 0.951 and boiled without appreciable decomposition at 300° to 310° C. under atmospheric pressure. Distillation of the calcium salt with an excess of soda-lime resulted in the production of a mixture of hydrocarbons boiling between 180° and 230° C., and having the average formula $C_{14}H_{26}$. These hydrocarbons, however, rapidly absorbed bromine so that the expected formation of a saturated cycloparaffin was not realized.

The naphthenic acids present in Rumanian kerosene were examined by von Frangopol,[53] who isolated hepta-, octa-, and nona-naphthenic acids besides smaller amounts of deca-, undeca-, and dodeca-naphthenic acids. Somewhat later Petrow[54] subjected the mixed methyl esters of naphthenic acids to careful fractionation and obtained the following fractions:

Fraction 1, boiling point 161° to 163° C. at 748 mm. and yielding on hydrolysis a free acid of boiling point 211° to 213° C. (heptanaphthenic acid?).

Fraction 2, boiling point 169° to 171° C. at 748 mm., yielding a free acid of boiling point 218° to 220° C. (methylcyclopentane-2-carboxylic acid?).

Fraction 3, boiling point 177° to 178° C. at 736 mm. (methyl ester of an octanaphthenic acid?).

Similarly a series of napthhenic acids from octanaphthenic acid up to pentadecanaphthenic acid (boiling from 236° up to 303° C.) was isolated by von Kozicki and von Pilat,[55] by distillation of the methyl esters of acids derived from Galician petroleum distillates. The crude acids were first purified by the method of Ardan,[56] which consists in adding low-boiling petroleum ether to an alcoholic solution of the mixed alkali naphthenates followed by isolation of the alkali naphthenates, free from neutral hydrocarbons, from the alcoholic solution.

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[51] *J.C.S.*, 1888, 53, 185.

[52] *Ber.*, 1888, 20, 596.

[53] Zur Kenntnis der Naphthensäuren aus rumänischen Erdöls, Diss. München, 1910.

[54] *J. Russ. Phys.-Chem. Soc.*, 1911, 43, 1198; *Chem. Zentr.*, 1912, 1, 1002.

[55] *Petroleum*, 1911, 11, 310; *Chem. Zentr.*, 1916, 1, 1145.

[56] Über Naphthene und Naphthensäuren, Diss. Karlsruhe, 1910.

The ethyl esters of naphthenic acids from Potok petroleum[57] yielded two fractions, one boiling at 95° to 170° C. (3 mm) and the other at 170° to 220° C. (3 mm). Reduction of these esters gave the alcohols, $C_{11}H_{22}O$ and $C_{17}H_{34}O$, respectively. Each alcohol was converted to the bromide, and these bromides on condensation with malonic ester, followed by treatment with urea and sodium ethylate, furnished the corresponding barbituric acid, $C_{16}H_{26}O_3N_2$ (m.p. 218°-220° C.) and $C_{22}H_{38}O_3N_2$ (m.p. 173°-177° C.). Reduction of ethyl naphthenates with sodium and ethyl alcohol in benzine resulted in the formation of a large proportion of glycols.

Zelinsky[58] made an attempt to settle the vexed question of the nature of the cycloparaffin ring present in the naphthenic acids. The acids from Baku petroleum were fractionated and converted into their methyl esters. From the lower-boiling portion of the esters, two fractions were isolated, having analytical compositions in accordance with those required for methyl heptanaphthenecarboxylate (octanaphthenate) and methyl octanaphthene carboxylate (nonanaphthenate), respectively, but the wide boiling range showed them to be mixtures of isomers. These fractions were reduced by sodium and alcohol to the corresponding primary alcohols, which were converted by iodine and red phosphorus into the iodides, and subsequently reduced by zinc dust to the hydrocarbon. The latter were saturated hydrocarbons, stable toward permanganate and concentrated sulphuric acid. When passed over platinum black at 300° C., conditions under which cyclohexane derivatives undergo thermal dehydrogenation, these hydrocarbons yielded very little hydrogen. It was concluded by Zelinsky that the original naphthenic acids cannot contain more than small amounts of cyclohexane derivatives. The main ring system is probably a cyclopentane ring. Investigation of the octa-, nona-, and deca-naphthene carboxylic acids in the same way showed that these also cannot contain more than a trace of cyclohexane derivatives.[59]

Von Braun[60] examined the naphthenic acids in distillates from Rumanian, Californian, Galician and German crudes and found that acids from these different sources exhibited the same characteristics, namely: those containing up to 6 or 7 carbon atoms were aliphatic, those possessing from 7 to 12 carbon atoms were monocyclic, while those which had more than 12 carbon atoms per molecule were dicyclic. No evidence was obtained for acids of more highly condensed systems. It was also observed that acids of approximately the same empirical composition occurred in the corresponding fractions from different crudes. Galician oils were exceptions in that the acids having more than 11 carbon atoms were aliphatic or monocyclic The low-molecular weight acids found in the distillates from Rumanian crudes were absent in the crude oil, from which largely secondary acids were isolated. This suggested that the low-molecular acids are the products of pyrogenic decomposition.

The work of Tanaka and his associates[61] was carried out on naphthenic acids derived from Japanese crudes as well as from a Californian distillate. The mixture of naphthenic acids was converted into methyl esters which were then

[57] von Pilat and Reyman, *Ann.*, 1932, 499, 76; *Brit. Chem. Abs.* **B**, 1932, 1262.

[58] Zelinsky, *Ber.*, 1924, *57B*, 42. *Cf.* Komppa, Routala and Kanerva, *Ber.*, 1929, **62**, 1562.

[59] Zelinsky and Pokrowskaja, *Ber.*, 1924, 57, 51.

[60] *Ann.*, 1931, 490, 100; *Brit. Chem. Abs.* **A**, 1931, 1396. *Natl. Pet. News*, 1932, 24 (8), 28; *Chem. Abs.*, 1932, 26, 4702.

[61] Tanaka and Nagai, *J. Fac. Eng. Tokyo Imp. Univ.*, 1924, 15, 271; *Chem. Abs.*, 1925, 19, 1135. Tanaka, Nagai and Ishida, *J. Fac. Eng. Tokyo Imp. Univ.*, 1924, 16, 8; *Chem. Abs.*, 1925, 19, 832. Tanaka and Nagai, *J. Fac. Eng. Tokyo Imp. Univ.*, 1925, 16, 171; *Chem. Abs.*, 1926, 20, 583; *J. Fac. Eng. Tokyo Imp. Univ.*, 1926, 16, 183; *Chem. Abs.*, 1926, 20, 2832; *J. Chem. Ind. Japan*, 1923, 26, 309; *ibid.*, 1923, 26, 1115; *Chem. Abs.*, 1924, 18, 2332; *J. Chem. Ind. Japan*, 1926, 29, 1; *Chem. Abs.*, 1926, 20, 985.

fractionated and the purified acids regenerated; or the mixed methyl esters were saponified to give the purified free acids which were submitted to fractionation. The most interesting result of this work from the structural point of view is that definite differences of density were found to exist between pure naphthenic acid fractions of the same boiling range but from different petroleums. Naphthenic acids from gas oil distillates of California (Long Beach and Santa Fé Springs) crudes had specific gravities somewhat lower than those derived from Kurokawa petroleum and a little higher than acids from Nishiyama petroleum. The explanation advanced for such facts is that two series of isomeric naphthenic acids, differentiated by specific gravities, exist and that the acids from Californian petroleum are probably a mixture of the two series of acids. All the acids appeared to be monocarboxylic acids of the formula $C_nH_{2n-2}O_2$. From the crude naphthenic acids of Echigo-Nishiyama petroleum, Tanaka and Nagai[62] isolated, by means of the methyl esters, a homologous series of acids from dodeca- to pentadecanaphthenic acids.

Komppa[63] isolated an undecanaphthenic acid, $C_{10}H_{19}COOH$, by fractionation of the methyl esters of naphthenic acids from Baku petroleum. The purified acid boiled at 271°-272° C. (764 mm.) and yielded ethyl and methyl esters boiling at 247°-248° C. (762 mm.) and 236°-237° C. (763 mm.), respectively. Reduction of the ethyl esters yielded an undecanaphthenol which was converted by phosphoryl chloride and phosphorus pentachloride into the corresponding chloride, $C_{10}H_{19}CH_2Cl$, boiling at 74° to 78° C. at 7 mm. This chloride, on reduction with sodium in alcohol, furnished an undecanaphthene $C_{11}H_{22}$, boiling point 183.5°-184.5° C. at 765 mm., d^{20}_{4} 0.81284 and n^{20}_{D} 1.44834, identical with the hydrocarbon found by Markownikow and Oglobin in Baku naphtha. Komppa concluded that the undecanaphthenic acid of the naphtha is a carboxylated derivative of the undecanaphthene hydrocarbon present in the same type of petroleum.

Carboxylic acids derived from lubricating fractions of Texas crudes have been described by Alleman,[64] who stated that these acids are not naphthenic acids proper since they do not conform to the equation $C_nH_{2n-2}O_2$. It is true that formerly the term naphthenic acid usually implied carboxylic acids of that general formula but later work, especially that of von Braun, has shown the essential artificiality of such a classification and has indicated the desirability of extending the term naphthenic acid to include not only monocyclic carboxylic acids of the formula $C_nH_{2n-2}O_2$ but also bicyclic and possibly polycyclic monocarboxylic acids ($C_nH_{2n-4}O_2$ and $C_nH_{2n-6}O_2$). In short, the term naphthenic acid is employed to designate all carboxylic acids which are to be found in crude petroleums, but more especially monocyclic acids of the formula $C_nH_{2n-1}COOH$ (or $C_nH_{2n-2}O_2$). The acids described by Alleman have 16 to 25 carbon atoms per molecule, molecular weights ranging from 250 to about 376, and belong predominantly to the series $C_nH_{2n-4}O_2$ and $C_nH_{2n-6}O_2$. One acid out of the eleven isolated from the mixed acids appeared to belong to the series $C_nH_{2n-8}O_2$. These acids are described as viscous liquids of high refractive index (1.48563 to 1.49654), distillable between 160° and 245° C. at 4 mm. but distilling with decomposition at ordinary pressure. Alleman is apparently the first investigator to obtain an indication of the existence in petroleum of bicyclic and tricyclic monocarboxylic acids, but the presence of the former was later firmly established by the work of von Braun.

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[62] *J.A.C.S.*, 1925, 47, 2369.

[63] Komppa, Routala and Kanerva, *Ber.*, 1929, 62, 1562.

[64] U. S. Patent 1,694,461, Dec. 11, 1928, assigned to Sun Oil Co.; *Chem. Abs.*, 1929, 23, 696.

TABLE 158.—*Naphthenic Acids (Monocyclic).*

Formula of Acid	Source from which Extracted	Constants of Acid Boiling Point ° C.	 Density	Boiling Point of Derivatives Methyl Ester ° C.	 Acid Chloride ° C.	Observer
$C_6H_{11}COOH$	Russian oil	215–217	d_{0}^{0} 0.9712	165.5–167.5	167–169	Aschan[a]
	Baku naphtha	211–213	—	161–163 (748 mm.)	—	Petrow[b]
	Baku naphtha	218–220	—	169–171 (748 mm.)	—	Petrow[b]
	Rumanian kerosene	216–220	d_{4}^{20} 0.9513	163–166	—	von Frangopol[c]
$C_7H_{13}COOH$	Russian oil	237–238	d_{20}^{20} 0.9830	189–190	193–195	Aschan[a]
	Baku naphtha	234–238	—	177–178	—	Petrow[b]
	Rumanian kerosene	234–238	d_{4}^{20} 0.9761	188–192	194–198	von Frangopol[c]
	Galician oil	236–238	—	185–193	192–196	von Kozicki and von Pilat[d]
$C_8H_{15}COOH$	Russian oil	251–253	d_{20}^{20} 0.9795	211–213	206–208	Aschan[a]
	Rumanian kerosene	248–252	d_{4}^{20} 0.9836	210–215	207–210	von Frangopol[c]
	Galician oil	250–253	—	210–214	206–212	von Kozicki and von Pilat[d]
$C_9H_{17}COOH$	Russian oil	255–260	—	220–225	—	Aschan[a]
	Rumanian kerosene	257–261	d_{4}^{20} 0.9851	223–226	214–217	von Frangopol[c]
	Galician oil	260–264	—	219–225	227–230	von Kozicki and von Pilat[d]
$C_{10}H_{19}COOH$	Rumanian oil	267–269	d_{0}^{0} 0.982	—	—	Hell and Medinger[e]
	Rumanian kerosene	263–266	d_{4}^{20} 0.9876	225–233	223–226	von Frangopol[c]
	Galician oil	255–258	—	205–210	215–219	von Kozicki and von Pilat[d]
	Baku naphtha	271–272	d_{4}^{20} 0.9707	236–237	106.5–108 (8 mm.)	Komppa[f]

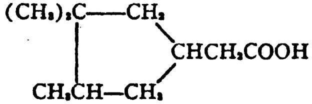
Formula of Acid	Source from which Extracted	Constants of Acid Boiling Point ° C.	Constants of Acid Density	Boiling Point of Derivatives Methyl Ester ° C.	Boiling Point of Derivatives Acid Chloride ° C.	Observer
$C_{11}H_{21}COOH$	Rumanian kerosene	272–272	d^{20}_{4} 0.9884	238–241	231–234	von Frangopol [c]
	Galician oil	268–272	—	226–230	228–234	von Kozicki and von Pilat [d]
	Nishiyama oil	168–170 (9 mm.)	d^{15}_{4} 0.9712	265–266	—	Tanaka and Nagai [f]
$C_{12}H_{23}COOH$	Alsatian oil	240–250 (140 mm.)	d^{15}_{15} 0.951	280–290	—	Krämer and Böttcher [g]
	Galician oil	272–275	—	235–240	238–241.5	von Kozicki and von Pilat [d]
	Nishiyama oil	177–179 (9 mm.)	d^{15}_{4} 0.9736	277–278	—	Tanaka and Nagai [f]
$C_{13}H_{25}COOH$	Galician oil	283–287	—	258–263	247–251	von Kozicki and von Pilat [d]
	Nishiyama oil	186–188 (9 mm.)	d^{15}_{15} 0.9762	289–290	—	Tanaka and Nagai [f]
$C_{14}H_{27}COOH$	Galician oil	300–303	—	280–290	283–287	von Kozicki and von Pilat [d]
	Alsatian oil	300–310	d^{15}_{15} 0.951	280–290	—	Krämer and Böttcher [g]
	Nishiyama oil	194–196 (9 mm.)	d^{15}_{4} 0.9776	300–301	—	Tanaka and Nagai [f]
$C_{19}H_{37}COOH$	——	310–320	—	300–301	—	Pyhälä [h]
$C_{24}H_{47}COOH$	——	ca. 340	d^{21}_{15} 0.9400	—	—	Pyhälä [h]

[a] *Ber.*, 1890, **23**, 871; 1891, **24**, 2723.
[b] *J. Russ. Phys.-Chem. Soc.*, **43**, 1198; *Chem. Zentr.*, 1912, 1, 1002.
[c] Dissertation, München, 1910.
[d] *Petroleum*, 11, 310; *Chem. Zentr.*, 1916, 1, 1145.
[e] *Ber.*, 1874, **7**, 1216; 1877, **10**, 451.
[f] *J.A.C.S.*, 1925, **47**, 2369; *J. Fac. Eng. Tokyo Imp. Univ.*, 1925, **16**, 171.
[g] *Ber.*, 1887, **20**, 595.
[h] *Z. angew. Chem.*, **27**, 407; *Chem. Rev. Fett- u. Harz-Industrie*, **21**, 128.
[i] *Ber.*, 1929, **62B**, 1562.

Naphthali[65] reported that the following acids have been isolated from Rumanian and Galician naphthenic acids:

$CH_3C_5H_8(CH_2)_2COOH$ $(CH_3)_2C_5H_7(CH_2)_2COOH$ $(CH_3)_3C_5H_6CH_2COOH$

The latter acid consists of a substance of the constitution



and is related to the 3,3,4-trimethylcyclopentanone obtainable from creosote oil.

The occurrence of aliphatic acids of the paraffin series has been noted by a number of workers. Tanaka and Kuwata[66] found that the crude petroleum acids derived from Ishikari (Hokkaido) gas-oil distillates contained, in addition to true naphthenic acids, a mixture (7.7 per cent of the total acids) of palmitic (4.5 parts), stearic (2 parts), myristic (2 parts), and arachidic acids (traces), which were separated by means of their lithium salts and subsequently the methyl esters. Similar fatty acids are said to occur in other Japanese petroleums, and also in those from California and Borneo. Crystals of arachidic acid were obtained by Holzmann and von Pilat,[67] by cooling the acid mixture extracted from a spindle oil. The presence of paraffin carboxylic acids in the lower fractions of Baku naphthenic acids was observed by Chichibabin.[68] Von Braun, as previously noted, has also found saturated acids of the formula $C_nH_{2n}O_2$ in the lowest fractions.

Before proceeding to discuss the results of von Braun it is desirable to tabulate the physical properties of the simple monocyclic naphthenic acids of the formula $C_nH_{2n-2}O_2$ which have been isolated by various workers from petroleums. It can hardly be doubted that these acids are mainly cyclopentane monocarboxylic acids, though many of the acids listed in Table 158 were probably not homogeneous chemical individuals and consisted of at least two isomers.

The work of von Braun has materially extended our knowledge of the chemical constitution of the naphthenic acids. The results obtained by previous workers seemed to indicate that the typical formula was $C_nH_{2n-2}O_2$ and that these acids were monocarboxylic acids derived from cycloparaffin hydrocarbons in which the COOH group was attached directly to the carbon ring. The work of Zelinsky and others, moreover, indicated that the ring system present was generally a cyclopentane ring. Von Braun[69] has shown as a result of his extensive experiments that these conclusions are erroneous in several particulars. It was found that the naphthenic acids are indeed monocarboxylic acids, derivatives mainly of cyclopentane and conform in general to the formula $C_nH_{2n-2}O_2$; but bicyclic saturated naphthenic acids of the empirical formula $C_nH_{2n-4}O_2$ also exist (possibly also polycyclic ones $C_nH_{2n-6}O_2$), while in the lowest fractions saturated aliphatic acids of the formula $C_nH_{2n}O_2$ occur. Von Braun concentrated his attention mainly on the question of the constitution of the monocyclic naphthenic acids of the formula $C_nH_{2n-2}O_2$, which were shown to consist not only of compounds of the type

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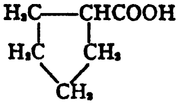
[65] *Z. angew. Chem.*, 1930, 43, 1051; *Chem. Abs.*, 1931, 25, 4857.

[66] *J. Fac. Eng. Tokyo Imp. Univ.*, 1928, 17, 293; *Brit. Chem. Abs.* B, 1929, 117.

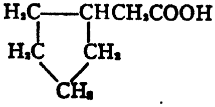
[67] *Brennstoff-Chem.*, 1931, 12, 41; *Brit. Chem. Abs.* B, 1931, 327.

[68] *Brennstoff-Chem.*, 1933, 14, 263; *Chem. Abs.*, 1933, 27, 5178. *Compt. rend. acad. sci. U.R.S.S.*, 1930A, 382; *Chem. Abs.*, 1931, 25, 2551; Chichibabin, Chirkov, Katznelson, Koryagin, and Chelintzev, *Bull. acad. sci. U.R.S.S. Classe sci. math. nat.*, 1932, 203; *Chem. Abs.*, 1932, 26, 3654; *Chimie et industrie*, Special No., March, 1932, 306. Also Lapkin, *Bull. inst. res. biol. Perm.*, 1931, 8, 51; *Brit. Chem. Abs.* B, 1933, 135.

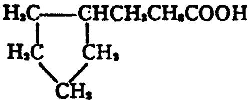
[69] *Allgem. Öl. u. Fettztg.*, 25, Mineralöle, 1, 13; *Chem. Zentr.*, 1929, 1, 2876; *Chem. Abs.*, 1930, 24, 3765; *Petroleum Z.*, 1931, 27, 673; *Chem. Abs.*, 1932, 26, 1102.



as was previously believed, but mainly of the types



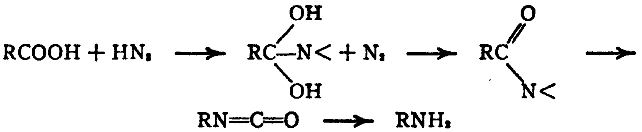
and



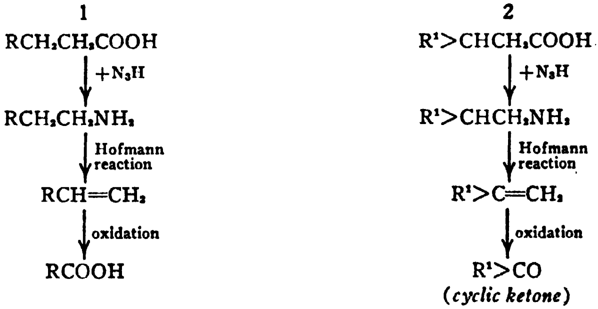
in which the carboxyl group is linked indirectly to the ring system through a chain of one, two, three, or even more, CH_2 groups. Direct evidence was also adduced that in the monocyclic naphthenic acids the ring structure involved is most frequently a cyclopentane ring.

The methods employed by von Braun in elucidating the structure of these acids are of sufficient interest to warrant a brief description. Three distinct methods of attack were employed.

(1) *The Amine-Olefin Method.* Treatment of a naphthenic acid with hydrazoic acid by the method of Schmidt leads to the formation of an amine (a naphthenamine) according to the reactions:



The naphthenamine, produced in 80 to 90 per cent yield by this method, can be readily purified through its oxalate or other salt and contains one carbon atom less than the parent naphthenic acid. Exhaustive methylation of this amine followed by the Hofmann degradation yields an olefin, which on oxidation with ozone furnishes *either* an acid with two carbon atoms less than the original naphthenic acid *or* a ketone with two carbon atoms less than the parent acid. These reactions are illustrated by the two following cases.[70]



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[70] The symbol $R^1{>}C$ indicates that the carbon atom forms a part of the cyclopentane structure contained in the radical R^1. This accounts for the formation of a ketone on oxidation.

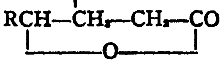
Obviously, if the parent naphthenic acid consists of a mixture of isomers of the two above-mentioned types, the series of reactions will result in the production of a mixture of an acid and a ketone easily separable by chemical means.

(2) *Progressive Degradation Method.* This method produces an acid with one carbon atom less than the parent naphthenic acid whereby a progressive degradation of the carboxylated side chain in the naphthenic acid molecule could be effected. The method is illustrated by the following case:

$$\begin{array}{l}
\mathrm{RCH_2COOH} \\
\Big\downarrow \text{ esterification} \\
\mathrm{RCH_2COOC_2H_5} \\
\Big\downarrow \text{ reduction} \\
\mathrm{RCH_2CH_2OH} \\
\Big\downarrow + \mathrm{HBr} \\
\mathrm{RCH_2CH_2Br} \\
\Big\downarrow + \mathrm{(CH_3)_3N} \\
\mathrm{RCH_2CH_2N(CH_3)_3Br} \\
\Big\downarrow \text{ decomposition of quaternary base} \\
\mathrm{RCH{=}CH_2} + \mathrm{(CH_3)_3N} + \mathrm{H_2O} \\
\Big\downarrow \text{ oxidation} \\
\mathrm{RCOOH}
\end{array}$$

(3) *Lactone Method.* In cases where the carboxyl group is linked to the ring through three CH_2 groups the following series of reactions lead to the formation of a lactone readily identifiable by oxidation.

$$\begin{array}{l}
\mathrm{RCH_2CH_2CH_2COOH} \\
\Big\downarrow \text{ esterification and bromination} \\
\mathrm{RCH_2CH_2CHBrCOOC_2H_5} \\
\Big\downarrow \text{ elimination of HBr} \\
\mathrm{RCH_2CH{=}CHCOOH} \\
\Big\downarrow \text{ rearrangement} \\
\mathrm{RCH{=}CHCH_2COOH} \\
\Big\downarrow
\end{array}$$

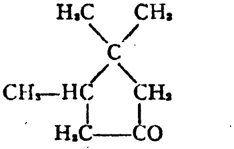


$$\underbrace{\mathrm{RCH{-}CH_2{-}CH_2{-}CO}}_{\mathrm{O}}$$

Lactone

Of the three methods of attack the most valuable are the first and second, which lead to a degradation of the side chain with the production of acids or ketones of lower molecular weight. By this process of progressively shortening the side chain the constitution of the side chain containing the carboxyl group can be definitely determined.

Von Braun has applied the above methods to the elucidation of the constitution of naphthenic acids of Rumanian, Galician, German, Californian, and Texan origin, with the following results. Investigation of *Galician* naphthenic acids showed that the acids boiling between 125° C. (12 mm.) and 210° C. (0.1 mm.) belong to the class of monocyclic acids. The fraction of boiling point 145°-150° C. (12 mm.) possessed the formula $C_9H_{17}COOH$ and was shown to consist of acids of the two types $C_7H_{13}CH_2CH_2COOH$ and $C_7H_{14}CHCH_2COOH$ since on treatment by Method 1 a mixture of ketones $C_7H_{14}CO$ and an acid $C_7H_{18}COOH$ was obtained. From the mixtures of ketones, a small amount of one having the following constitution (as shown by later work)[71] was obtained:



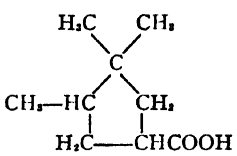
3,3,4-trimethylcyclopentanone-1

The fraction boiling from 190° to 200° C. (12 mm.) of Galician naphthenic acids was proved to contain a monocyclic acid of the formula $C_{13}H_{25}CH_2COOH$, since on degradation by Method 1 it yielded a monocyclic ketone, $C_{12}H_{24}{>}CO$. The fraction boiling from 195° to 205° C. (0.1 mm.) corresponded with the formula $C_{18}H_{34}O_2$ and was proved to contain a monocyclic acid of the formula $C_{14}H_{27}CH_2CH_2CH_2COOH$ by the lactone method.

Examination of Rumanian naphthenic acids by von Braun yielded the following results.

Fraction boiling from 118° to 127° C. at 12 mm. contained a mixture of various monocyclic acids of 7 and 8 carbon atoms.

Fraction boiling from 139° to 140° C. at 12 mm. contained several isomeric acids of the formula $C_8H_{15}COOH$. A small proportion of these acids was of the $C_7H_{14}CHCOOH$ type, such as the acid



but a greater proportion contained acids of the type $C_7H_{13}CH_2COOH$. Degradation of the latter acid by Method 1 resulted in the production of an acid $C_6H_{11}COOH$ and a ketone $C_6H_{12}{>}CO$, so that both the molecular types of $C_6H_{11}CH_2CH_2COOH$ and $C_6H_{12}{>}CHCH_2COOH$ were present.

Fraction boiling from 150° to 155° C. at 12 mm. ($C_9H_{17}COOH$) was examined exhaustively by all the three methods outlined previously. Method 3—the lactone method—showed the presence of acids of the type $C_6H_{11}CH_2CH_2CH_2COOH$ containing isomeric methylcyclopentyl residues. The use of Method 2 resulted in the formation of a mixture of isomeric acids of the type $C_8H_{15}COOH$, this demonstrating the absence in the original acids of any acids in which the carboxylic group is linked directly with the cyclic system. Finally, Method 1 yielded an acid of the formula $C_7H_{13}COOH$ (derived from an original acid of the type $C_7H_{13}CH_2CH_2COOH$) and a mixture of ketones, $C_7H_{14}>CO$, in which was identified a compound of the formula

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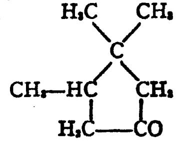
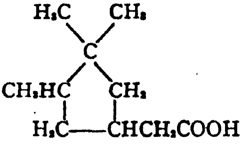
[71] Von Braun, Mannes and Reuter, *Ber.*, 1933, 66, 1499.



This ketone could only have been derived from a $C_{10}H_{18}O_2$ acid of the formula



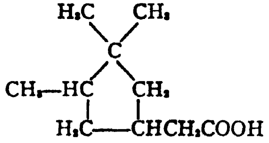
which is also present in the C_{10} acids of Galician and Californian naphthenic acids. Summarizing, it can thus be inferred that in this fraction of $C_{10}H_{18}O_2$ acids, molecules of the type $C_6H_{11}CH_2CH_2CH_2COOH$, $C_7H_{13}CH_2CH_2COOH$, and $C_8H_{15}CH_2COOH$ were present, but no acids containing a carboxyl group linked directly to the cyclic system.

The fraction boiling from 180° to 200° C. at 12 mm. of Rumanian acids corresponded to the formula $C_{14}H_{24}O_2$ and was evidently bicyclic. Conversion into the amine $C_{13}H_{23}NH_2$ and then into olefin $C_{13}H_{22}$, followed by oxidation, yielded ultimately a bicyclic ketone $C_{11}H_{20}>CO$ so that the original acid possessed the constitution $C_{11}H_{20}>CHCH_2COOH$. The character of the bicyclic system involved has not been determined.

Fraction boiling from 200° to 220° C. at 12 mm. ($C_{16}H_{28}O_2$) contained a bicyclic acid which yielded, by a treatment similar to that described above, a bicyclic ketone of the formula $C_{13}H_{24}>CO$.

Fraction boiling from 220° to 240° C. at 12 mm. of the formula $C_{18}H_{32}O_2$, furnished another bicyclic ketone of the formula $C_{15}H_{28}>CO$.

Californian Naphthenic Acids. *The fraction boiling from 145° to 155° C. at 12 mm.* consisted of monocyclic C_{10} acids which yielded, by Method 1, a mixture of monocyclic ketones, $C_7H_{14}>CO$. In this ketone mixture it was found possible to identify 3,3,4-trimethylcyclopentanone so that the original acid mixture undoubtedly contained an acid of the structure



as well as other isomeric acids with a $-CH_2COOH$ side chain.

Fraction boiling from 162° to 172° C. at 12 mm. contained monocyclic C_{12} acids. Conversion into the amine $C_{11}H_{21}NH_2$ and olefin $C_{11}H_{20}$, followed by oxidation, furnished a mixture of ketones of the formula $C_9H_{18}>CO$, from which a single individual ketone, $C_{10}H_{18}O$, was extracted. This ketone is isomeric with menthane and contains a five-membered ring.

Fraction boiling from 180° to 200° C. at 12 mm. possessed the formula $C_{13}H_{22}O_2$, and degradation by the amine method yielded a bicyclic ketone, $C_{11}H_{18}O_2$.

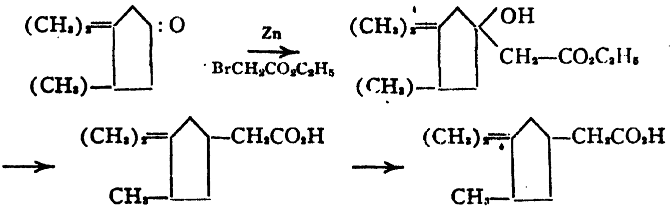
Fraction boiling from 200° to 220° C. at 12 mm. consisted of bicyclic monocarboxylic acids of the formula $C_{14}H_{24}O_2$. The usual amine degradation furnished a mixture of bicyclic ketones, $C_{11}H_{20}>CO$, from which a single individual was isolated which proved to be identical with the ketone derived from the $C_{14}H_{24}O_2$ acids of Rumanian naphthenic acids. Both the original acids, therefore, possessed the constitution $C_{12}H_{21}CH_2COOH$, in which the $C_{12}H_{21}-$ radieal represents a bicyclic hydrocarbon residue.

The fraction boiling from 260° to 280° C. at 12 mm. from Rumanian petroleum constituted the highest molecular weight acids isolated by von Braun. This fraction consisted of bicyclic acids of the formula $C_{20}H_{36}O_2$.

Examination of naphthenic acids in Texas crudes showed that the acid fractions with 12 carbon atoms were monocyclic while the higher fractions contained only bicyclic acids.

The results of von Braun indicate that Rumanian, German, Californian, and Texan naphthenic acids consist of both monocyclic and bicyclic monocarboxylic acids, the bicyclic acids preponderating in the higher fractions with 13 and 14 carbon atoms. In the case of the Galician acids, however, the monocyclic types appear to persist even in fractions as high as C_{18} fractions, these being the highest monocyclic acids encountered by von Braun. Tri- and polycyclic acids have not yet been identified in the fractions so far examined, but their existence is indicated by the work of Alleman and Maitland.

Later, von Braun, Mannes and Reuter[72] prepared a pure naphthenic acid, 3,3,4-trimethylcyclopentylacetic acid. This acid was formed from 3,3,4-trimethylcyclopentanone-1. The course of the synthesis is indicated by the following:



CHEMICAL AND PHYSICAL PROPERTIES OF NAPHTHENIC ACIDS

Crude naphthenic acids from different crude oils and distillates vary greatly in physical and chemical characteristics. Acids of low molecular weight such as those obtained from Baku petroleum are volatile oils of penetrating odor, while high molecular weight acids such as those obtained from lubricating stocks are viscous, and in some cases semi-solid, materials. Crude acids frequently contain relatively large amounts of foreign substances including neutral compounds and resins and for this reason often exhibit an iodine absorption value. However, all purified naphthenic acids appear to be fully saturated substances so that the iodine values of crude acids is a sign of their contamination with foreign materials. In Table 159 will be found Pyhälä's[73] data on the properties of various commercial naphthenic acids from Baku petroleum:

TABLE 159.—*Properties of Commercial Naphthenic Acids from Baku Petroleum.*

Source of Acid	Acid No.	d^{15}	Iodine No.	Viscosity at 30° C.
Kerosene	255	0.9650	0.9	4.23° Engler
Same	230	0.9504	2.62	—
Light solar oil	170.0	0.9513	2.42	15.00° E
Vaseline oil	152.0	0.9471	—	—
Heavy solar oil	136.0	0.9418	2.50	18.96° E
Spindle oil	108.0	0.9358	6.17	34.76° E
Machine oil	87.5	0.9350	7.18	47.71° E
Cylinder oil	32.6	0.9294	11.36	97.92° E

In many instances crude acids are of a very dark color, particularly those from the higher fractions of petroleum. Schwarz and Marcusson[74] described a crude naphthenic acid from Russian lubricating stock which was a brownish-black, thick, oily liquid with an acid number of 118.3 and an iodine number (Waller) of 5.5, soluble in benzine and containing much combined sulphur. Acids from Galician and Rumanian lubricating stocks were brownish-black resinous substances, soluble in benzine, and having acid numbers of 87.6 and 157.4, respectively.

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[72] *Ber.*, 1933, 66, 1499.

[73] *Z. angew. Chem.*, 1914, 27, 1, 407; *Chem. Abs.*, 1915, 9, 1842; *Chem. Rev. Fett- u. Harzindustrie*, 1914, 21, 128; *Chem. Abs.*, 1914, 8, 2800; *Petroleum*, 1914, 9, 1373; *Chem. Abs.*, 1914, 8, 3361; *Chem.-Ztg.*, 1912, 36, 869; *Chem. Abs.*, 1912, 6, 3381; *Petroleum*, 1914, 9, 1506; *Chem. Abs.*, 1915, 9, 372; see Budowski, "Die Naphthensäuren," Julius Springer, Berlin, 1922, 30.

[74] *Chem. Rev. Fett.- u. Harzindustrie*, 1908, 15, 165; *Chem. Zentr.*, 1908, 2, 352.

The acids obtained from American lubricating stocks by the Alleman process[75] are dark in color and have an acid number of 103, but the acid numbers of the distilled acids is generally higher. For example, distillation of the acids under 4 mm. pressure yielded the following fractions:

Boiling Range °C. (4 mm.)	Acid No.
Up to 180	187
180–190	174.4
190–200	160
Residue (containing resins)	61

Other acids, obtained by hydrolyzing the naphthenic soaps with steam under pressure followed by acidification with hydrochloric acid and distillation under reduced pressure, were very dark in color and had an acid number of 85. Acids obtained in the same way, but further purified by means of alcohol, had an acid number of 124 and were of a light amber color. These are polycyclic monocarboxylic acids containing 16 to 25 carbon atoms, and are low-melting viscous oils.

Purified naphthenic acids from various sources also exhibit a wide variation in physical properties, but their chemical properties are more uniform and differ only in degree. A large number of purified naphthenic acid fractions (most of which undoubtedly contained mixtures of isomers and frequently of homologues) have been described. All these acids appear to be colorless, or faintly colored oily liquids, distillable unchanged at 200° to 300° C. and volatile in steam. Their densities are all less than 1 but appear to decrease with increasing molecular weight—at least in the case of the monocyclic acids of the formula $C_nH_{2n-2}O_2$. They are insoluble or sparingly soluble in water, but are soluble in hydrocarbons and in many organic solvents. Their viscosities increase with increasing molecular weight, while their surface tensions decrease.[76] They exert a corrosive action on many metals especially lead, zinc, copper, and tin, but aluminum is resistant to their action.[77] Corrosion of refinery equipment due to naphthenic acids has been reported by Vuiborova.[78]

Despite statements to the contrary, it seems that the simple monocyclic acids dissolve readily in concentrated sulphuric acid but may be precipitated unchanged by addition of water.[79] A remarkable case of irreversible adsorption of naphthenic acids by fuller's earth has been recorded by Gurwitsch,[80] who found that filtration of the acids through this material resulted in the adsorption of about 6 per cent which could not be extracted from the adsorbent by organic solvents.

The antiseptic properties of the (monocyclic) naphthenic acids, exhibited also by many of their salts, was noted by Charitschkow,[80a] who ascribed this property to the presence of a cyclopentyl ring since benzoic and hexahydrobenzoic acids do not possess antiseptic powers. The subject was further investigated by Spalwing,[80b] who found that 1 per cent of free acids, or their salts in a concentration of 1:100, exerted as powerful an effect on various pathogenic organisms as 3 per cent of phenol. The free acids appear to be the most effective, followed by their copper, iron, zinc, and aluminum salts in the order of their activities. According to Kupsis,[80c] the naphthenic acids exhibit toxic properties particularly toward fish. That the toxicity of some crude petroleums and residues is destroyed by washing with alkali indicates that such toxicity is due to their naphthenic acid content.

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[75] U. S. Patents 1,694,462 and 1,694,463, Dec. 11, 1928, assigned to Sun Oil Co.; *Chem. Abs.*, 1929, 23, 697.

[76] Goldberg and Gurwitsch, *Aserb. Neft. Khoz.*, 1928, No. 5, 46; *Chem. Abs.*, 1928, 22, 3767.

[77] Budowski, "Die Naphthensäuren," Julius Springer, Berlin, 1922.

[78] Vuiborova, *Neft. Khoz.*, 1930, 9, 117; *Brit. Chem. Abs.* B, 1931, 284.

[79] Schulz, *Chem. Ztg.*, 1908, 32, 772; *Chem. Abs.*, 1908, 2, 2954.

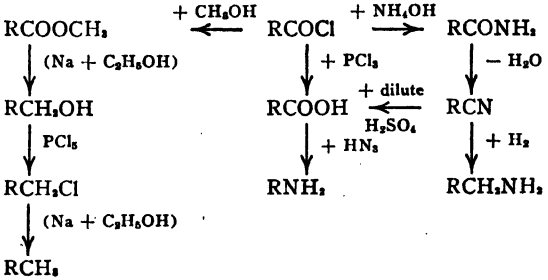
[80] *Z. physik. Chem.*, 1914, 87, 323; *Chem. Abs.*, 1914, 8, 2090; *Petroleum*, 1912, 8, 65; *Chem. Abs.*, 1913, 7, 1602.

[80a] *Z. angew. Chem.*, 1899, 739; *J.S.C.I.*, 1899, 18, 852.

In chemical properties the naphthenic acids exhibit the characteristic properties of monocarboxylic saturated aliphatic acids. They are stable and do not combine additively with halogens. Under certain conditions, however, they are attacked by bromine with the formation of bromine substituted compounds accompanied by the evolution of hydrogen bromide. Their ease of esterification by aliphatic alcohols in the presence of a catalyst, such as concentrated sulphuric acid or hydrogen chloride, has already been mentioned and a considerable number of such esters, more especially the methyl esters, have been prepared. It is interesting to note that dimethyl sulphate (or other dialkyl sulphates) may be used for esterification of these acids.[81] The methyl and ethyl esters of the monocyclic acids are oily liquids possessing somewhat fruity odors. Esters of naphthenic acids with glycerol have also been prepared by heating three molecules of the acid with one molecule of glycerol to 250° C. for several hours.[82] Reduction of the methyl or ethyl esters by the method of Bouveault and Blanc leads to the production of a primary alcohol.[83] For example, the reduction of the ethyl ester of undecanaphthenic acid (from Baku petroleum) by sodium and ethyl alcohol resulted in the formation of the corresponding alcohol, undecanaphthenol, boiling point 236.5°-237.5° C.[84]

$$C_{10}H_{19}COOC_2H_5 + 2H_2 \longrightarrow C_{10}H_{19}CH_2OH + C_2H_5OH$$

A considerable number of simple derivatives of the monocyclic acids containing 7 to 14 carbon atoms have been prepared by various workers and their formation may be summarized in the following scheme:



$$\begin{tikzcd}
RCOOCH_3 \arrow[d, "(Na + C_2H_5OH)"] & RCOCl \arrow[l, "+ CH_3OH"'] \arrow[r, "+ NH_4OH"] \arrow[d, "+ PCl_3"] & RCONH_2 \arrow[d, "- H_2O"] \\
RCH_2OH \arrow[d, "PCl_5"] & RCOOH \arrow[d, "+ HN_3"] & RCN \arrow[l, "+ \text{dilute}"', "H_2SO_4"] \arrow[d, "+ H_2"] \\
RCH_2Cl \arrow[d, "(Na + C_2H_5OH)"] & RNH_2 & RCH_2NH_2 \\
RCH_3 & &
\end{tikzcd}$$

Of the derivatives of the monocyclic acids, the amides are white crystalline solids and the acid chlorides are liquids which can be distilled without decomposition at 200° to 260° C. The two amines produced according to the above scheme are strongly basic liquids with an ammoniacal odor. In this connection it is interesting to note that the salts of the amine $C_{19}H_{35}NH_2$ produced from the bicyclic acids, $C_{20}H_{36}O_2$, of a higher fraction (boiling from 250° to 270° C. at 12 mm.) of Rumanian naphthenic acids were found (by von Braun) to possess marked emulsifying properties in aqueous solution, just like solutions of the alkali salts of the higher fatty acids except that the former react acid in solution. Arylamino derivatives of naphthenic acids have been prepared by reacting the acids with aromatic amines.[84a] On sulphonation the sulphonic acid group is said to enter the aromatic ring of such compounds.

[80b] *Farmazeft*, 1903, 11, 191; *Chem.-Ztg.*, 1903, 27, Rep. 196.

[80c] *Pharmaz. Zentralhalle*, 1902, 43, 217; *Chem. Zentr.*, 1902, 1, 1171.

[81] Von Kozicki and von Pilat, *Petroleum*, 1916, 11, 310; *Chem. Zentr.*, 1916, 1, 1145; *Chem. Abs.*, 1916, 10, 2296.

[82] Budowski, "Die Naphthensäuren," Julius Springer, Berlin, 1922.

[83] Petrow, *J. Russ. Phys.-Chem. Soc.*, 1911, 43, 1198; *Chem. Zentr.*, 1912, 1, 1002.

[84] Komppa, Routala and Kanerva, *Ber.*, 1929, 62, 1562.

The work of von Braun has furnished numerous methods of converting these acids into other substances such as amines,[84b] ketones and lower acids, and will no doubt lead to an extension of our knowledge of hydrocarbons possessing a cyclopentane ring and possibly also of saturated bicyclic hydrocarbon structures.

The possibility of converting naphthenic acids into ketones, which may be utilized as solvents, has engaged the attention of a number of workers. Stadnikov and Donde[85] made use of the method of Grün,[86] which consists in heating high-boiling organic acids to a temperature of 200° to 300° C. Caucasian naphthenic acids, boiling between 140° and 190° C. at 25 mm., were introduced drop by drop into a reaction tube containing a catalyst of ferric oxide on asbestos. The acids were unchanged at 360° to 370° C., but at 450° C. underwent a reduction of acid number from 220 to 47 and the catalyst was soon rendered inactive. From 525 grams of naphthenic acid there were finally obtained 340 grams of a product with an acid value of 94, consisting of a mixture of unsaturated hydrocarbons and oxygenated compounds in which ketones were only present in an insignificant amount. Greater success was achieved by Zelinsky and Rjachina,[87] who passed a mixture of acetic acid and mixed naphthenic acids, from Balachany (Caucasus) petroleum, over a catalyst of mixed manganous and zinc oxides at 410° to 420° C. and obtained as a product a mixture of acetone, ketones derived from naphthenic acids and acetic acid, and ketones derived from naphthenic acids only. The reactions, in which RCOOH represents a naphthenic acid, may be represented as:

$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$
$$R.COOH + CH_3COOH \longrightarrow RCOCH_3 + CO_2 + H_2O$$
$$2RCOOH \longrightarrow RCOR + CO_2 + H_2O.$$

Passage of a mixture of 240 grams of naphthenic acids (boiling from 235° to 250° C.) and 304 grams of acetic acid quickly over the above catalyst at 410° to 420° C. yielded 170 grams of crude ketones and 110 grams of unchanged acids. Slower passage of a mixture of 430 grams of naphthenic acids with 500 grams of acetic acid over the same catalyst at the same temperature furnished 470 grams of ketones and only 29 grams of unchanged acids.

The ketones regenerated from the bisulphite compounds were mixtures of isomers derived from the acids C_5H_9COOH, $C_7H_{13}COOH$, and $C_8H_{15}COOH$, and acetic acid. The following ketones are described by Zelinsky and Rjachina, all of the type $C_nH_{2n-1}COCH_3$:

[84a] Soc. des produits chimiques et matières colorantes de Mulhouse, French Patent 711,952, 1930; *Chem. Abs.*, 1932, **26**, 1943.

[84b] *Cf.* Schmidt, German Patent 500,435, 1928; *Chem. Abs.*, 1932, **26**, 2198; German Patent 544,890, 1930; *Chem. Abs.*, 1932, **26**, 3515; both patents assigned to Knoll A.-G. Chem. Fab.

[85] *Trans. Karpov Inst. Chem.*, 1925, No. 4, 188; *Chem. Abs.*, 1926, **20**, 2152.

[86] German Patent 295,657, 1914; *J.S.C.I.*, 1917, **36**, 569.

[87] *Ber.*, 1924, **57B**, 1932; *Chem. Abs.*, 1925, **19**, 647.

$C_7H_{12}O$ b.p. 177°–184° C., semicarbazone m.p. 105°–107° C.

$C_8H_{14}O$ b.p. 184°–190° C., d^{15}_{4} 0.8836, semicarbazone m.p. 135° C.

$C_9H_{16}O$ b.p. 204°–207° C., d^{15}_{4} 0.8921, semicarbazone m.p. 142° C.

$C_{10}H_{18}O$ b.p. 210°–212° C., d^{21}_{4} 0.8861, semicarbazone m.p. 140° C.

The ketones which did not combine with sodium bisulphite were separated by distillation into a series of fractions each containing a large number of isomers. Ketones boiling from 190° to 207° C. were derived from the naphthenic acids, $C_7H_{13}COOH$. Those boiling in the ranges, 207° to 210° C., 212° to 215° C. and 220° to 235° C., corresponded with the acids $C_8H_{15}COOH$, $C_9H_{17}COOH$, and $C_{10}H_{19}COOH$, respectively.

The formation of small amounts of ketones by the oxidation of crude naphthenic acids (of acid number 267) in ammoniacal solution with hydrogen peroxide has been noted by Naphthali.[88] Beckman[89] described a method of producing ketones from naphthenic acids which consists in passing the oil vapors through two reaction chambers containing lime. The first chamber is maintained at 200° C. and the second at 400° C. Ketones of the formula $C_nH_{2n}O$ are said to be formed.

The cracking of naphthenic acids under pressure in the presence of water and alumina has been investigated by Ipatiew and Petrov.[90] The products consisted of acetone, acetic and formic acids in the aqueous layer and an oily layer containing paraffinic, naphthenic and unsaturated hydrocarbons, ketones, and naphthenic and paraffinic acids. The following three reactions were suggested to explain the various products: (1) Splitting off of the carboxyl group with the formation of a naphthene which may be further degraded; (2) formation of lower molecular weight naphthenes by fission of the side chain containing the carboxyl group; and (3) formation of fatty acids from the carboxylated side chains so eliminated.

APPLICATIONS OF NAPHTHENIC ACIDS

The most important use of naphthenic acids is in the manufacture of soaps, detergent compositions, greases and water-soluble oils, for which purposes the sodium salts are most frequently employed.[91] A number of other metallic salts have also found important application for various purposes. The free naphthenic acids have been proposed as suitable solvents for vulcanized rubber,[92] various resins and gums such as copal, dammar, sandarac, and mastic,[93] and for aniline dyes.[94] According to Petit,[95] the viscosities of concentrated colloidal solutions (generally containing at least one organic solvent) can be reduced, without further modification of their properties, by the addition of naphthenic acids. It was stated that the fluidity of printing inks may be improved by the addition of these acids.[96] Their use in clarifying agents for petroleum oils has been suggested by Swartz.[96a] Evans [96b] recommended nitrated or sulphonated naphthenic acids for breaking petroleum emulsions. Pyhälä [96c] described the separation of crude-oil emulsions with naphthenic acids. The incorporation of 5 to 40 per cent by volume of naphthenic acids with hydrocarbons to yield motor fuels is described by Kleinschmidt.[97] Sulphonation of these acids with chlorosulphonic acid gives materials which are cleansing, emulsifying and wetting agents.[98] Materials with similar properties can also be made by condensing sulphonated naphthenic acids with amines, amino acids, or aminoalcohols.[98a] Naphthenesulphonic acids have been recommended as catalysts in the preparation of acrolite resins.[98b] Transparent sheets have been made from gelatin, a mineral oil, and sulphonated naphthenic acids.[98c] Naphthenic glycerides have been recommended as ingredients of coating compositions for stencil sheets.[99] A mixture prepared by heating at 240° C. oleic acid (which had been preliminarily heated to 150° C.), seal or cod-liver oil, naphthenic acids and sufficient glycerol for esterification, has been suggested for removing fats from hides.[99a] The free acids have been proposed as constituents for insecticides.[100] Addition of about 15 per cent of naphthenic acids to wood (tung) oil prevents gelatinization during heating and a thick clear oil is obtained which dries without cracking or yielding a web-like formation.[101] The free acids can also be incorporated in detergent compositions,[102] and esters of the bromo- or chloroacids or cyclohexyl esters [102a] of naphthenic acids may be employed as plasticizers.[103] The penetrating or wetting power of mercerizing lyes can be improved by the addition of naphthenic acids,[104] the naphthenic esters of the lower monohydric alcohols,[105] or of naphthenic alcohols obtained by the reduction of the corresponding acids.[106] Alcohols containing more than three hydroxyl groups (e.g., pentaerythritol) are esterified with a mixture of naphthenic and resin acids and then blown with air or vulcanized.[107] The products may be used as coating compositions or in the preparation of lacquers.

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[88] *Chem. Umschau*, 1926, **33**, 1; *Chem. Abs.*, 1926, **20**, 2151.

[89] U. S. Patent 1,753,642, April 8, 1930; *Chem. Abs.*, 1930, **24**, 2590.

[90] *Brennstoff-Chem.*, 1930, 175; *Ber.*, 1930, **63B**, 329.

[91] For a review of the use of naphthenic acids in soap making, see Schuck, *Mat. Grasses*, 1922. **14**. 6249; *Chem. Abs.*, 1923, **17**, 220. For the preparation of oil-water emulsions and of greases, see Ubbelohde, German Patent 261,070, 1910; *Chem. Abs.*, 1913, **7**, 3226; Frizell and Stagner, U. S. Patent 1,582,257, Apr. 27, 1926; assigned to Union Oil Co. of California; *Chem. Abs.*, 1926, **20**, 2067.

[92] Chercheffsky, German Patent 218,225, 1908; *Chem. Abs.*, 1910, **4**, 1813; Kinney, U. S. Patent 1,815,778, July 21, 1931; assigned to Standard Oil Co. of Indiana; *Chem. Abs.*, 1931, **25**, 5595.

[93] Radcliffe and Pollitt, *J. Soc. Dyers and Colourists*, 1916, **32**, 160; *Chem. Abs.*, 1916, **10**, 2301; *Seifensieder-Z.*, 1916, **43**, 884.

[94] Cassidy, U. S. Patent 1,860,850, May 31, 1932; *Chem. Abs.*, 1932, **26**, 3915.

[95] French Patent 686,880, 1929; *Chem. Abs.*, 1931, **25**, 785.

Naphthenic alcohols are obtained by reduction of naphthenic acids with hydro-

[96] Hollins and Chapman, British Patent 279,968, 1926; *Chem. Abs.*, 1928, **22**, 3055.

[96a] U. S. Patent 1,878,650, Sept. 20, 1932; assigned to Jenkins Petroleum Process Co.; *Chem. Abs.*, 1933, **27**, 408.

[96b] U. S. Patent 1,856,156, May 3, 1932; *Brit. Chem. Abs.* **B**, 1933, 259.

[96c] *Erdöl u. Teer*, 1930, 6, 478; *Chem. Abs.*, 1931, **25**, 2276.

[97] British Patent 185,796, 1921; *Chem. Abs.*, 1923, **17**, 335.

[98] Chem. Fabrik Milch, A.-G., British Patent 275,267, 1926; *Chem. Abs.*, 1928, **22**, 2284. Klein, German Patent 566,767, 1928; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1933, **27**, 2570.

[98a] Dreyfus, British Patent 390,166, 1931; *Brit. Chem. Abs.* **B**, 1933, 617; British Patent 394,657, 1931; *Brit. Chem. Abs.* **B**, 1933, 857

[98b] Petrov and Schmidt, *Plast. Massi*, 1931, 1, 27; *Brit. Chem. Abs.* **B**, 1932, 356.

[98c] Kratz, U. S. Patent 1,847,656, Mar. 1, 1932; assigned to Marsene Products Co.; *Chem. Abs.*, 1932, **26**, 2561.

[99] Horii, U. S. Patent 1,792,095, Feb. 10, 1931; *Chem. Abs.*, 1931, **25**, 1958; U. S. Patent 1,799,793, Apr. 7, 1931; *Chem. Abs.*, 1931, **25**, 3139; U. S. Patent 1,829,750, Nov. 3, 1931; *Chem. Abs.*, 1932, **26**, 816. See also Alvarado and Parrett, Canadian Patent 331,634, 1933; assigned to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, **27**, 3836.

[99a] Velikovskii, Russian Patent 24,935, 1932; *Chem. Abs.*, 1932, **26**, 3696.

[100] I. G. Farbenindustrie A.-G., German Patent 526,179, 1927; *Chem. Abs.*, 1931, **25**, 4352. Also Merrill, U. S. Patent 1,695,197, Dec. 11, 1928; assigned to Union Oil Co. of California; *Chem. Abs.*, 1929, **23**, 697.

[101] "Vernisol," Soç. Anon. Fabrique de Vernis et Produits isolants pour l'Industrie Electrique in Vevey (Schweiz), German Patent 253,845, 1912. A similar use of naphthenic acids with castor oil is described by Scheiber; German Patent 555,496, 1929; *Chem. Abs.*, 1932, **26**, 5223.

[102] Zick, U. S. Patent 1,812,507, June 30, 1931; assigned to Standard Oil Development Co.; *Chem. Abs.*, 1931, **25**, 5054.

[102a] Deutsche Hydrierwerke A.-G., British Patent 390,534, 1931; *Brit. Chem. Abs.* **B**, 1933, 662.

[103] Dreyfus, British Patent 390,541, 1931; *Brit. Chem. Abs.* **B**, 1933, 503.

[104] Chemische Fabrik vorm. Sandoz, French Patent 40,615, 1931; *Chem. Abs.*, 1933, **27**, 1523; addition to 624,174.

[105] Pospiech, U. S. Patent 1,917,326, July 11, 1933; assigned to Chemische Fabrik Potts and Co.; *Chem. Abs.*, 1933, **27**, 4692.

[106] Erba Fabr. Chem. Produkte Spezialitäten f. die Textilind., British Patent 394,499, 1932; *Brit. Chem. Abs.* **B**, 1933, 864.

[107] I. G. Farbenindustrie A.-G., British Patent 351,945, 1929; *Brit. Chem. Abs.* **B**, 1931, 853.

gen under pressure in the presence of heavy metal naphthenates.[108] Another procedure consists in treating naphthenic esters with metallic sodium and an alcohol.[109] Chlorination or sulphonation (with chlorosulphonic acid) of these alcohols yields materials which are wetting, emulsifying or dispersing agents;[110] or the alcohol may first be converted to the chloride (with hydrochloric acid) and afterwards heated (under pressure) to 150° to 180° C. with an aqueous-alcoholic solution of sodium sulphite.[111]

THE NAPHTHENIC ACID SOAPS AND THEIR USES

Of the salts of the naphthenic acids, the sodium soaps are by far the most important. The commercial sodium soaps usually possess the consistency of greases but the purified soaps of the lower monocyclic acids are frequently crystalline solids. Thus, sodium octanaphthenate has been described as a non-hygroscopic solid, crystallizable without water of crystallization. The sodium salts of the monocyclic acids are soluble in water but their solubility decreases with increasing molecular weight of acid. They may be salted out of solution with common salt, but not as readily as the soaps derived from coconut oil and other vegetable acids.[112] Furthermore, the naphthenic acid soaps are hydrolyzed in aqueous solution only to a very slight extent as compared with the fatty acid soaps.[112] The naphthenic soaps combine excellent emulsifying and foam-producing properties with a low hydrolytic dissociation and therefore are of value as mild detergents, for example for use in the textile industries. The power possessed by naphthenic soap solutions of readily forming emulsions with water-insoluble mineral oils has been referred to. Gurwitsch[113] found that the solubility of the oil increases as the concentration of the soap in the aqueous solution is increased and with increasing molecular weight of naphthenic acid used, but decreases with rising temperature. The dissolved oil is removed only with the greatest difficulty by shaking with petroleum ether, and is not precipitated by free naphthenic acids, but is easily separated by the addition of an equal volume of alcohol. The indications are, therefore, that solutions of mineral oils in naphthenic acid soap solutions are the result of adsorption of the oil on the micelles of the soap.

The properties of a sodium soap prepared from a mixture of Japanese naphthenic acids (d_4^{15} 0.9708 and acid number 249.2) have been described by Mikumo,[114] more especially with reference to surface and interfacial tensions and emulsifying, lathering and detergent properties. The naphthenic acid soap was extremely soluble in cold water and was superior to coconut oil soap in lathering power. It was, however, soft and far inferior to an oleate soap in detergent action, and appeared to occupy a position intermediate between fatty and rosin soaps.

Kawakami[115] examined the properties of the sodium salt of mixed naphthenic acids (boiling between 195° and 200° C. at 10 mm., d_{15}^{25} 0.9605, mean molecular weight 246.5 and acid number 228.0) which was used in the soap industry. The detergent action and lathering power of the naphthenic soap were compared with those of sodium palmitate and mixed toilet soap, the latter two proving to be a little superior to the former. The gelation capacity of the sodium naphthenate was found to be extraordinarily great. Cooling a 40 per cent aqueous solution of this soap to 0° C. for 30 minutes did not cause complete solidification, thus demonstrating its applicability in neutral soft and liquid soaps. Larger amounts of common salt were required to salt the sodium naphthenate out of aqueous solution than in the case of a coconut oil soap. The sodium naphthenate was hydroscopic in moist air.

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[108] Deutsche Hydrierwerke A.-G., British Patent 396,311, 1932; *Brit. Chem. Abs.* **B**, 1933, 836.
[109] Deutsche Hydrierwerke A.-G., German Patent 552,535, 1930; *Chem. Abs.*, 1932, **26**, 5780.
[110] I. G. Farbenindustrie A.-G., British Patent 394,043, 1932; *Brit. Chem. Abs.* **B**, 1933, 823.
[111] Deutsche Hydrierwerke A.-G., British Patent 369,301, 1931; *Brit. Chem. Abs.* **B**, 1932, 671.
[112] Davidsohn, *Z. angew. Chem.*, 1914, **27**, 1; *Chem. Abs.*, 1914, **8**, 1024.
[113] *Kolloid-Z.*, Spec. No. April 1, 1925, p. 196; *Chem. Abs.*, 1925, **19**, 2898.
[114] *J. Soc. Chem. Ind. Japan*, 1925, **28**, 1121; *Brit. Chem. Abs.* **B**, 1926, 286.
[115] *J. Soc. Chem. Ind. Japan*, 1926, **29**, 64; *Chem. Abs.*, 1926, **20**, 2422.

White and Knopf[116] described a gear lubricant (having a MacMichael viscosity of 70 to 85 poises at 38° C.) comprising an oxidized light lubricating oil, heavy flux and sodium naphthenates substantially free from water. Rudigier[117] proposed to compound a heavy residual oil containing sodium naphthenates with a mineral lubricating distillate of viscosity 65 to 200 sec. (Saybolt) at 38° to yield a product of viscosity above 125 sec. (Saybolt) at 100° C. and a pour test not above 3° C. Velikovskii[117a] prepared greases by heating small proportions of lead oxides with naphthenic acids to about 270° C. under increased pressure together with fatty acids, glycerol and castor oil in the presence of iron. To eliminate separation of constituents in greases made from naphthenic soaps and mineral oils,[117b] he proposed converting the naphthenic acid into its glycerol ester, which is saponified in the subsequent heating.

The property of sodium naphthenates of stabilizing oil-water emulsions may be employed in the manufacture of benzene, and other hydrocarbon, emulsions in water for use as detergents, defatting agents or spraying compositions,[118] as well as emulsions of asphaltic substances which are applicable as paving materials or binding agents.[119] In the preparation of some of these products the marked disinfectant properties of the naphthenic acid soaps are of considerable value.[120] The addition of 6 to 8 per cent sodium naphthenates to an alkaline cold-swelling starch produces a dry painters' size which does not deteriorate on storage.[121] Graphite mixed with a solution of gum tragacanth, triethanolamine, and a small proportion of sodium naphthenates gives a lubricant.[122]

OTHER NAPHTHENIC ACID SALTS

A general method of preparation of the calcium and heavy metal salts of the naphthenic acids consists in mixing an aqueous solution of an alkali naphthenate with a solution of a salt of calcium or heavy metal.[123] Thus, by the addition of a solution of calcium chloride to an alkali naphthenate solution, the calcium naphthenate is usually precipitated by double decomposition:

$$2RCOONa + CaCl_2 \longrightarrow (RCOO)_2Ca + 2NaCl$$

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[116] U. S. Patent 1,789,614, Jan. 20, 1931; assigned to Sinclair Refining Co.; *Chem. Abs.*, 1931, **25**, 1375.

[117] U. S. Patent 1,750,134, Mar. 3, 1930; assigned to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1931, 56.

[117a] Russian Patent 23,521, 1931; *Chem. Abs.*, 1932, **26**, 2049.

[117b] Velikovskii, Russian Patent 26,395, 1931; *Chem. Abs.*, 1932, **26**, 6119.

[118] Simon and Dürkheim, German Patent 309,574, 1916; *J.S.C.I.*, 1919, **38**, 295A.

[119] Hack, Australian Patent 21,709, 1929; assigned to Colitho Pavements Pty., Ltd.; *Chem. Abs.*, 1931, **25**, 5539. Pree, German Patent 537,792, 1927; *Chem. Abs.*, 1932, **26**, 1459.

[120] Davidsohn, *Seifensieder-Z.*, 1909, **36**, 1552; *Chem. Abs.*, 1911, **5**, 798. Burstin, German Patent 319,199, 1918; *Chem. Abs.*, 1921, **15**, 605. Saposhnikow and Kopythovski, *Neft. Khoz.*, 1926, **11**, 748; *Chem. Abs.*, 1928, **22**, 3276.

[121] W. A. Scholten's Chem. Fabrik, British Patent 346,220, 1930; *Brit. Chem. Abs.* **B**, 1931, 737; French Patent 696,635, 1930; *Chem. Abs.*, 1931, **25**, 2823. Chem. Fabrik Mahler and Supf A.-G., German Patent 556,448, 1929; *Chem. Abs.*, 1932, **26**, 5777.

[122] Thomsen and O'Laughlin, U. S. Patent 1,895,014, Jan. 24, 1933; assigned to Joseph Dixon Crucible Co.; *Chem. Abs.*, 1933, **27**, 2572.

[123] Cherchewsky, *Seifensieder-Z.*, 1911, **38**, 765; *Chem. Abs.*, 1912, **6**, 1224. I. G. Farbenindustrie A.-G., British Patent 335,863, 1929; *Chem. Abs.*, 1931, **25**, 1841.

The calcium and barium salts of the monocyclic acids are obtained either in the form of crystalline solids or as viscous pasty masses. They are soluble to a slight extent in water, insoluble in hydrocarbons, but usually somewhat soluble in alcohol. The calcium salts have been proposed as constituents of various fats and greases and for the manufacture of water-soluble oils or cutting compounds. The calcium salt of the polycyclic acid, obtained from American crudes by the Alleman process,[124] are light sticky tenacious masses practically insoluble in water. They are very soluble in ethyl acetate, carbon tetrachloride, gasoline, benzene, or ether, dissolve to some extent in turpentine and linseed oil, but are only slightly soluble in ethyl and methyl alcohols and acetone. The calcium salts may be used in waterproofing compositions, adhesives, wood fillers, grafting waxes, cements, varnishes, etc. The barium and calcium salts are particularly useful, however, in the preparation of color lakes to be used in the manufacture of lithographic and printing inks, colored paints, and varnishes.[125]

A considerable number of metallic naphthenates have been described and some of these are of technical importance. In connection with the double decomposition method of preparation used by practically all workers, it has been pointed out that precipitation is best carried out at the boiling temperature of the solution and that the precipitate may be dried at 130° C.[126] Of the salts of the *monocyclic acids,* the copper compounds are remarkable in that they dissolve in benzine, yielding a green solution.[127] This reaction (the so-called Charitschkoff test) has been used as a method of identification of naphthenic acids.[127a] Most of the heavy metal salts are amorphous solids, frequently highly colored, are only slightly soluble in water, but dissolve in hydrocarbons. A number of salts of trideca-, tetradeca-, and pentadeca-naphthenic acids have been prepared by Tanaka, Horiuchi, and Oyama.[128] The lead salts are transparent resinous solids. The manganese tridecanaphthenate is a pink powder, soluble in ether but practically insoluble in hot or cold water. Aluminum naphthenates are transparent colorless porous masses, the magnesium and zinc salts being white powders. Chromium salts were obtained in two modifications, namely, a violet powder at temperatures below 40° C. transformed into a green viscous mass by warming. The solubilities of the salts decrease with increasing molecular weight of acid. According to Yamada,[129] the solubilities of metallic oleates and naphthenates are on the whole very similar. Exceptions are mercury and lead naphthenates which are easily soluble in alcohol at 5° C. (over 33 per cent and 29 per cent, respectively), while the corresponding oleates are practically insoluble. Again, acetone at 5° C. dissolves over 22 per cent of zinc naphthenate but less than 0.4 per cent zinc oleate.

A number of the metallic salts of the (monocyclic) acids have found application in industry and arts. Copper naphthenate is a wood preservative[130] as well as an insecticide and fungicide.[131] The copper salt may be prepared by decomposing sodium naphthenate with copper sulphate in aqueous solution. It is soluble in gasoline and mineral oil distillates and may be applied in the form of these solutions. The zinc[132] and lead[133] salts may also be employed as wood preservatives. Solutions of aluminum naphthenates in organic solvents, with or without the addition of wetting agents, are said to be insecticides.[134] Metallic naphthenates, e.g., those of zinc, magnesium and lead, which are difficultly soluble in water, have been proposed as insulating materials.[135] According to Yamada,[136] the addition of 0.1 per cent of tin naphthenate to transformer oils exerts an inhibitory effect on sludge formation. Deterioration of lubricating oils in service is lessened by the addition of mercury naphthenates.[137] Lead naphthenates have been suggested as drying agents in varnishes,[138] as a catalyst[138a] for the reaction between unsaturated fatty acids and sulphites in the presence of air, and as substances for admixture with lubricating oils to produce "chatterless" oils.[139] Mercury compounds of naphthenic acids or their esters are said to be antiknock ingredients.[140] The use of chromium and aluminum naphthenates as siccatives is described by Ruth and Asser.[141] An emulsion of ammonium naphthenate and solvent naphtha can be employed for spraying plants, and is said to be less harmful than free naphthenic acids or their alkali or alkaline-earth salts.[142] Lead, zinc or tin naphthenates, together with a small proportion of aluminum naphthenate, can be melted with a small amount of ceresin, naphthenic acid glycerides and castor or mineral oil to give insecticides.[143]

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[124] U. S. Patents 1,694,462 and 1,694,463, Dec. 11, 1928; assigned to Sun Oil Co.; *Chem. Abs.,* 1929, **23**, 697.

[125] Alleman, U. S. Patent 1,781,772, Nov. 18, 1930; assigned to Sun Oil Co.; *Chem. Abs.,* 1931, **25**, 420. The use of calcium naphthenates as drying-oil substitutes is described by Gurvich, Russian Patent 26,393, 1928; *Chem. Abs.,* 1932, **26**, 6164.

[126] I. G. Farbenindustrie A.-G., British Patent 335,863, 1929; *Chem. Abs.,* 1931, **25**, 1841.

[127] Charitschkoff, *J. Russ. Phys.-Chem. Soc.,* 1897, **29**, 691; *Chem. Zentr.,* 1898, 1, 1191.

[127a] Luft (*Petroleum Z.,* 1932, **28** (24), 16; *Chem. Abs.,* 1932, **26**, 4706; *Brit. Chem. Abs.* **B**, 1932, 760) examined the sensitiveness of this test in the presence of various substances.

[128] *J. Chem. Ind. Japan,* 1923, **26**, 1190; *Chem. Abs.,* 1924, **18**, 2688.

[129] *J. Chem. Ind. Japan,* 1930, **33**, 412; *Brit. Chem. Abs.* **B**, 1931, 500.

[130] von Wolneiwicz, *Chem. Ztg.,* 1889, **13**, 1089; *J.S.C.I.,* 1889, **8**, 874.

[131] Rogers and McNeil, U. S. Patent 1,679,919, Aug. 7, 1928; assigned to Standard Oil Co.; *Chem. Abs.,* 1928, **22**, 3728.

An interesting application of the heavy metal salts (particularly the cobalt, manganese, and lead salts) in the form of their solutions in the fatty acids of drying or non-drying oils[144] or in mixtures of fatty acids and drying oils[145] is as paint and varnish driers. The so-called "Soligen" driers consist of such solutions of heavy metal naphthenates (from Russian naphthenic acids), particularly the cobalt salts. According to Stock,[146] linseed oil varnishes containing 0.14 per cent to 0.29 per cent of cobalt, as naphthenates, dry in 1 to 10 per cent less time than those containing a resinate drier. Petrov[146a] suggested the addition of heavy metal salts of naphthenic acids to improve the odor of petroleum distillates.

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[132] Charitschkoff, *Petroleum,* 1909, 5, 92; *Chem.-Ztg.,* 1909, 33, 595.

[133] I. G. Farbenindustrie A.-G., British Patent 322,768, 1928; *Brit. Chem. Abs.* **B**, 1930, 370.

[134] Alleman, U. S. Patent 1,781,772, Nov. 18, 1930; *Chem. Abs.,* 1931, 25, 420; U. S. Patent 1,818,778, Aug. 11, 1931; *Chem. Abs.,* 1931, 25, 5576.

[135] I. G. Farbenindustrie A.-G., British Patent 335,863, 1929; *Chem. Abs.,* 1931, 25, 1841. A volatile solvent (e.g., benzene) may be added to the acids before the drying step: British Patent 367,666, 1930; *Chem. Abs.,* 1933, 27, 1893. *Cf.* Meidert, U. S. Patent 1,878,962, Sept. 20, 1932; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.,* 1933, 27, 434; British Patent 380,360, 1932; *Brit. Chem. Abs.* **B**, 1932, 1115; British Patent 383,172, 1932; *Brit. Chem. Abs.* **B**, 1933, 78.

[136] *J. Chem. Ind. Japan,* 1930, 30, Suppl. Binding, 318; *Chem. Abs.,* 1930, 24, 5997.

[137] Ducamp, British Patent 368,025, 1931; *Brit. Chem. Abs.* **B**, 1932, 459.

[138] I. G. Farbenindustrie A.-G., German Patent 510,937, 1927; *Chem. Abs.,* 1931, 25, 1108; British Patent 353,783, 1929; *Chem. Abs.,* 1932, 26, 3685; British Patent 370,550, 1931; *Brit. Chem. Abs.* **B**, 1932, 614. *Cf.* Ducamp and Baule, U. S. Patent 1,932,156, Oct. 24, 1933; British Patent 383,856, 1932; *Chem. Abs.,* 1933, 27, 4427.

[138a] Ott and Schüssler, German Patent 551,424, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.,* 1932, 26, 4494.

[139] Doell and Klemgard, U. S. Patent 1,781,167, Nov. 11, 1930; assigned to Standard Oil Co. of California; *Chem. Abs.,* 1931, 25, 201. Rosenbaum, U. S. Patent 1,860,622, May 31, 1932; *Chem. Abs.,* 1932, 26, 3916. *Cf.* Velikovskii, Russian Patent 23,521, 1931; *Chem. Abs.,* 1932, 26, 2049.

[140] Rosenbaum, U. S. Patent 1,841,254, Jan. 12, 1932; *Chem. Abs.,* 1932, 26, 1768.

[141] German Patents 327,374, and 327,375, 1919; *J.S.C.I.,* 1921, 40, 187A.

[142] I. G. Farbenindustrie A.-G., German Patent 433,653, 1922; *Brit. Chem. Abs.* **B**, 1927, 233.

[143] Velikovskii, Russian Patents 21,286, 1929, and 25,224, 1931; *Chem. Abs.,* 1933, 27, 1446.

[144] I. G. Farbenindustrie A.-G., British Patent 339,865, 1929; *Chem. Abs.,* 1931, 25, 2865; British Patent 383,172, 1932; *Chem. Abs.,* 4428.

[145] I. G. Farbenindustrie A.-G., British Patent 339,922, 1929; *Chem. Abs.,* 1931, 25, 2865; British Patent 364,836, 1931; *Chem. Abs.,* 1933, 27, 2050; British Patent 397,276, 1932; *Chem. Abs.,* 1933, 27, 879. Schatz, German Patent 546,771, 1930; assigned to I. G. Farbenindustrie A.-G.; *Chem. Abs.,* 1932, 26, 3686. The use of Soligen drier or of various naphthenates in varnish and paint is discussed by Kogan and Churdenko, *Farben-Ztg.,* 1932, 27, 1664; *Brit. Chem. Abs.* **B**, 1932, 927; Klebsattel, *Paint, Oil and Chem. Rev.,* 1932, 93 (14), 11; *Chem. Abs.,* 1932, 26, 3122; Carrier, *Amer. Paint and Varnish Mfg. Assoc.,* Dec. 1931, *Circ.* 404, 635; *Brit. Chem. Abs.* **B**, 1932, 195; Pickard, *Amer. Paint and Varnish Mfg. Assoc.,* Dec. 1931, *Circ.* 404, 542; *Brit. Chem. Abs.* **B**, 1932, 195.

[146] *Seifensieder-Z.,* 1931, 58, 144.

[146a] German Patent 570,564, 1933; *Chem. Abs.,* 1933, 27, 4386.

The copper, chromium, and nickel salts of the (polycyclic) naphthenic acids, obtained from American lubricating stocks by the Alleman and Maitland processes,[147] are green in color and may be used as paints. The cobalt salt, which is purple, can be used in a similar manner. The manganese salt is mahogany in color and hardens on exposure to air.

The heavy metal salts have also been suggested as ingredients of rust-proof coating compositions for metals,[148] particularly those containing benzyl cellulose, as preservatives for threads, cordage and textiles,[149] and as agents to reduce or suppress the viscosity or sticky nature of asphalts.[150] Refined petroleum asphalts, mixed with natural or synthetic resin and iron naphthenate, can be employed in the manufacture of rubberized cloth.[151]

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[147] *Loc. cit.* See also Potolovskii, Russian Patent 30, 1923; *Chem. Abs.*, 1929, **23**, 5051; Gerlach, U. S. Patent 1,875,999, Sept. 6, 1932; *Chem. Abs.*, 1933, **27**, 199.

[148] Schladerbach and Hähle, U. S. Patent 1,844,983, Feb. 16, 1932; German Patent 570,738, 1933; *Chem. Abs.*, 1933, **27**, 4427; both patents assigned to I. G. Farbenindustrie A.-G.

[149] Landmark and Nagel, Norwegian Patent 49,855, 1931; *Chem. Abs.*, 1933, **27**, 1524.

[150] Bataafsche Petroleum Maatschappij, British Patent 355,430, 1930; *Brit. Chem. Abs.* **B**, 1931, 1037; French Patent 718,507, 1931; *Chem. Abs.*, 1932, **26**, 3372.

[151] E. I. duPont de Nemours and Co., French Patent 41,067, 1931; *Chem. Abs.*, 1933, **27**, 1524; addition to 693,890, 1930; *Chem. Abs.*, 1931, **25**, 1687.

Chapter 49

Analysis of Natural Gas and Cracking Gas

The methods ordinarily employed for the analysis of the usual industrial gaseous fuels, such as coal gas and producer gas, are not generally applicable to the precise analysis of natural petroleum gases or of gases obtained during the pyrolysis of hydrocarbons, e.g., in commercial cracking operations. This is because of the fact that the two types of petroleum gases often contain very large proportions of several individual gaseous hydrocarbons which are difficult to separate from one another on a laboratory scale. Thus, natural gas usually contains large proportions of methane together with ethane, propane, butanes, and even higher paraffin hydrocarbons, whereas the analysis of cracking gas is still further complicated by the presence of unsaturated hydrocarbons, as well as of hydrogen. With the exception of carbon dioxide and hydrogen sulphide, which often occur to some extent in natural petroleum gases, none of the constituents of natural gas can be estimated by the rapid and accurate absorption methods used for other industrial gases. Moreover, the analysis of industrial gases (e.g., coal gas) is not beset by the necessity of separating a number of homologous hydrocarbons, since methane is their preponderant hydrocarbon constituent.

The importance of accurate and reliable methods for the analysis of the complex gas mixtures encountered in the petroleum industry cannot be overemphasized. Analytical control of the natural-gasoline extraction industry has made possible the accurate assessment of plant efficiency, establishing scientific control of operations which were formerly governed more or less empirically.[1] The need of reliable analytical data relating to hydrocarbon gases is also obvious in some of the newer applications of such materials in industry, e.g., in the large-scale fractionation of hydrocarbon gases for the isolation of one or more constituents in a substantially pure condition. The increasing importance of unsaturated constituents of cracking gas in chemical synthesis, particularly the utilization of gaseous monolefins in the production of alcohols, makes it imperative to use reliable analytical methods. The development of procedures for the analysis of complex hydrocarbon mixtures has greatly facilitated the progress of research in certain branches of petroleum chemistry, especially the scientific study of pyrolytic reactions.

The following discussion is intended primarily as a brief account of the general methods available for the analytical investigation of hydrocarbon gas mixtures but it will also be necessary to refer, cursorily, to the estimation of certain non-hydrocarbon constituents of petroleum gases, most important of which are carbon dioxide, hydrogen sulphide, and, in the gases from cracking operations, hydrogen and carbon monoxide.[1a] It will be understood that most of the analytical methods discussed in this chapter are subject to a degree of experimental error which is probably never less than ±0.1 per cent and frequently much greater.

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[1] See Burrell, "The Recovery of Gasoline from Natural Gas," Chemical Catalog Co., Inc., New York, 1925.

[1a] Carbon monoxide may be produced from petroleum gases, for example, in the catalytic high-temperature decomposition of hydrocarbons in the presence of steam, as discussed in Chapter 10.

In the analysis of coal gas and allied gases, two main methods of procedure have been employed, namely, absorption and combustion (or explosion). Later, methods for the analysis of hydrocarbon gas mixtures made use of a third mode of operation, that of low-temperature fractionation (or in some cases, fractional condensation). Besides the above, several special methods, which depend upon the accurate determination of various physical constants, are available for the estimation of hydrocarbons in mixtures. However, since these latter methods are only applicable in general to mixtures of two (or, at most, of three) components, their value in the investigation of natural and cracking gases is limited.

ANALYSIS BY ABSORPTION

The first methods available for the analysis of gases depended upon the removal of an individual constituent or group of components of the mixture by appropriate liquid reagents in a definite order. From the quantity of gas removed after each absorption, the composition of the mixture was determined. The choice of absorbing liquids is frequently a somewhat difficult one, particularly for unsaturated hydrocarbons. Some of the reagents employed in gas analysis are capable of absorbing several constituents. However, by adopting a definite order of absorption it is possible to eliminate this difficulty to a large extent.

It is not necessary in a work of this scope to enter into a detailed description of the various types of apparatus employed for gas analysis by absorption. In brief, the usual method is to measure the volume of the gas at constant pressure in a eudiometer (gas burette) enclosed in a water-jacket (for temperature control) and supplied with a levelling device containing mercury, water, or other liquid (for pressure control). The gas is forced into a pipette containing the absorbent liquid where it remains for a definite period, after which it is withdrawn and its volume re-measured. Other constituents are removed and their volumes determined in the same manner. The percentage composition can be calculated from the losses in volume on absorption. One of the simplest forms of apparatus for absorption gas analysis is that of Orsat, of which numerous modifications and improvements have been elaborated.[2] In other forms of apparatus, somewhat different methods are employed. Bone and Wheeler [3] described an apparatus which combined a high degree of accuracy with a number of other advantages.[4] In this apparatus changes in the pressure of the gas at constant volume after absorption are observed instead of changes in volume at constant pressure, as in other methods. By this procedure, greater accuracy and faster manipulation are attainable. In the Orsat apparatus, for example, the absorptions are generally carried out in a number of large pipettes, each containing a particular reagent which is used again in successive analyses. On the other hand, in the Bone and Wheeler apparatus the absorptions are carried out in a vessel over mercury, with a comparatively small volume (2 to 5 cc.) of fresh reagent, which is discarded after use. By this method not only is the reagent fresh each time it is used, but the minimum quantity is employed, thus minimizing possible errors resulting from solution of other gaseous constituents in a large volume of liquid.

[2] A precise form of Orsat Apparatus, developed at the U. S. Bureau of Mines, is described in *U. S. Bur. Mines Bull.* **197** (1926); see also Shepherd, *Bur. Standards J. Research,* 1931, **6**, 121; *Chem. Abs.,* 1931, **25**, 1455.

[3] *J.S.C.I.*, 1908, **27**, 10.

[4] For a detailed description of the Bone and Wheeler apparatus, see Blair and Wheeler, *J.S.C.I.,* 1922, **41**, 187T; also Grice and Payman, *Fuel,* 1924, **3**, 236; *Chem. Abs.,* 1924, **18**, 3296.

Reagents for the absorption of the constituents of gas mixtures are described below in the order of their use in analysis. The period of contact of gas with reagent depends upon the amount to be absorbed and the activity of the reagent, but, in general, 2 to 5 minutes is sufficient.

Carbon dioxide is absorbed in a concentrated aqueous solution of potassium hydroxide, prepared by dissolving 500 grams (one pound) of stick potassium hydroxide (not that described as "purified by alcohol") in 500 cc. of distilled water. This reagent also absorbs hydrogen sulphide[5] and other acid constituents. Ambler[5a] used "ascerite" for the absorption of carbon dioxide.

Acetylene is best estimated by absorption in Lebeau's reagent,[6] an alkaline solution of potassium mercuric iodide, prepared by dissolving 25 grams of mercuric iodide and 30 grams of potassium iodide in 100 cc. of water. A small quantity of solid potassium hydroxide is added to this solution immediately prior to the absorption.

Several other reagents have been employed for the absorption of acetylene, for example, ammoniacal cuprous and silver salt solutions.[7] Since they also absorb olefins, diolefins, carbon monoxide, and other gases to some extent, they can have only a limited application.

Oxygen is estimated by absorption in an alkaline solution of pyrogallol, prepared immediately before use by adding a concentrated potassium hydroxide solution to about one-fourth of its volume of an aqueous solution of pyrogallol (28 grams in 100 cc. of water) in the absence of air.

Unsaturated hydrocarbons are next absorbed either in a dilute solution of bromine in fuming sulphuric acid or in concentrated sulphuric acid containing 1 per cent of silver sulphate. In this way the total unsaturated hydrocarbon content is obtained. An account of the analytical separation of the individual olefins is given later.

For the determination of the total unsaturated gases with bromine water, a saturated solution of bromine in 5 per cent aqueous potassium bromide is usually recommended but this solution should be diluted at least twice when mercury is used in the apparatus since mercury is attacked by the reagent. Oberseider and Boyd[8] found that bromine water has a tendency to attack paraffin hydrocarbons (in cracking gases) on exposure to daylight or artificial light. To overcome this a blackened absorption pipette was suggested. After the unsaturated constituents have been absorbed in bromine water, the gas must be washed with potassium hydroxide solution to remove bromine vapor.

Fuming sulphuric acid is a rapid absorbent for all olefins, but it also slowly absorbs paraffin hydrocarbons.

Carbon monoxide is absorbed in an ammoniacal cuprous chloride solution, prepared by passing ammonia gas into a suspension of 75 grams of pure cuprous chloride in 200 cc. of distilled water containing 25 grams of ammonium chloride in solution until all the cuprous salt has dissolved. The reagent must be freshly prepared and kept out of contact with air. For the complete removal of carbon monoxide at least two absorptions with fresh reagent are necessary. The gas is then washed with 5 per cent sulphuric acid to remove ammonia vapor before the gas volume is measured. Even after two or three treatments with ammoniacal cuprous chloride, small quantities of carbon monoxide often remain in the gas.

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[5] Hydrogen sulphide is best estimated in a separate analysis. The determination of hydrogen sulphide and organic sulphur is discussed in Chapter 50.

[5a] *Analyst,* 1931, 56, 635; *Brit. Chem. Abs.* A, 1931, 1391.

[6] Lebeau and Damiens, *Compt. rend.,* 1913, 156, 557; *Chem. Abs.,* 1913, 7, 1468.

[7] See, for example, Hague and Wheeler, *J.C.S.,* 1929, 383; Morris, *J.A.C.S.,* 1929, 51, 1460.

[8] *Ind. Chem. Eng., Anal. Ed.,* 1931, 3, 123.

These traces [8a] may be estimated (as carbon dioxide) in the subsequent combustions of hydrogen over copper oxide.

Blacet, MacDonald and Leighton [8b] described a method for the microanalysis of gases by absorption with dry reagents instead of liquids. Yellow phosphorus is used for absorbing oxygen, potassium hydroxide for carbon dioxide, fused phosphorus pentoxide for water, silver oxide for carbon monoxide, fuming sulphuric acid for ethylene, and a mixture of cuprous chloride and potassium hydroxide for acetylene.

As a method for the analysis of air, Pozner and Melikova [8c] suggested the absorption of unsaturated hydrocarbons in lead acetate, aromatic hydrocarbons in sulphuric acid containing silver, and paraffins and naphthenes by activated charcoal.

ANALYSIS BY COMBUSTION AND EXPLOSION

The gas, after removal of the absorbable constituents, contains paraffin hydrocarbons, hydrogen and nitrogen. In the analysis of coal gas and other similar gases, in which the preponderating paraffin gas is methane, the determination of this residual gas is a comparatively simple matter. The hydrogen is preferentially oxidized to water either by copper oxide at 280° C. or by palladium sponge at 100° C. and the residual methane-nitrogen mixture (containing only small amounts of ethane) is then exploded with excess of air as described below. When the gas consists principally of methane with smaller proportions of ethane and practically no higher homologues, this gives sufficient data for calculating the proportions of hydrogen, nitrogen, and paraffin hydrocarbons. However, with natural and cracking gases, in which a number of homologous paraffin hydrocarbons are present, the above method is not directly applicable. It therefore becomes necessary to effect some fractionation of the constituents. A number of procedures for fractionating such mixtures of homologous gaseous paraffins on an analytical scale are discussed later. It is sufficient here to note that a simple low-temperature condensation procedure is capable of separating the hydrogen, nitrogen, and methane (as one fraction) from the residual homologues of methane. This mixture of hydrogen, nitrogen, and methane may then be submitted to treatment as described below.

Estimation of Hydrogen. In a mixture of hydrogen, nitrogen and paraffins (mainly methane), the hydrogen may be quantitatively estimated by taking advantage of its relatively much greater ease of oxidation. The hydrogen is eliminated as water and the reduction in volume (or, in pressure at constant volume) of the gas corresponds to the hydrogen content. A method developed for this purpose by King [9] consists in passing the gas mixture very slowly over fresh copper oxide maintained at a temperature of 280° C. in a silica tube. This treatment effects a complete and rapid oxidation of hydrogen and leaves the methane unattacked. The treatment is continued until no further diminution of volume occurs, which usually requires about 30 minutes. If any carbon monoxide is present in the gas, under these conditions it is oxidized to carbon dioxide, which may be estimated in the usual way. This method is satisfactory for gas mixtures containing methane as the main gaseous paraffin constituent. Ethane and its higher homologues, on the other hand, are oxidized slowly in this manner, and therefore, in the presence of large proportions of these constituents, the method is unreliable. The oxidation of ethane may be minimized by operating at 250° C. but, at this temperature, the hydrogen oxidation proceeds rather slowly.

[8a] Booth and Campbell (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 131) determined traces of carbon monoxide in ethylene by means of the reaction of the former with oxygenated blood. The change in the oxygenated blood is measured colorimetrically after the addition of a mixture of equal parts of pyrogallic and tannic acids.

[8b] *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 266, 272.

[8c] *J. Applied Chem. Russia,* 1931, 4, 932; *Chem. Abs.*, 1932, 26, 1877.

[9] *Fuel*, 1922, 1, 103; *Chem. Abs.*, 1922, 16, 3600. See also King and Edgcombe, *Dept. Sci. and Ind. Research, Fuel Research, Tech. Paper* 33, 1931; *Brit. Chem. Abs.* B, 1932, 215; *Chem. Abs.*, 1932, 26, 4160.

The other method which has been previously mentioned consists of a preferential elimination of the hydrogen by oxidation in the presence of "oxidized" palladium sponge at 100° C. On being heated to a dull red heat, palladium sponge undergoes superficial oxidation and then has the property, when maintained at 100° C., of removing hydrogen and leaving the paraffin hydrocarbons untouched. Its action is partly oxidation and partly occlusion. The palladium sponge requires fairly frequent re-oxidation by heating in contact with air. The details of this method have been described by Grice and Payman.[10]

According to Rischbieth,[11] hydrogen may be completely separated from methane by passing the mixture together with air over a palladium wire heated almost to glowing.

Hydrogen may also be quantitatively absorbed by a colloidal solution of palladium, as described by Paal and Hartmann[12] and by Beet.[13] Hague and Wheeler[14] carried out hydrogen estimations by this method at a temperature of 50° C., employing an absorption time of 30 minutes.

Determination of Paraffin Hydrocarbons by Oxidation.—Several methods are available for the analysis of the nitrogen and paraffin hydrocarbon mixture remaining after removal of the absorbable gases and hydrogen. All of them depend upon the complete oxidation of the paraffins to carbon dioxide and water. The volume of the carbon dioxide produced from a given volume of the mixture is measured by absorption in potassium hydroxide solution. The residual gas may then be considered to consist of nitrogen, helium and other inert gases.

It is important to note that complete combustion methods of analysis of mixtures of paraffin hydrocarbons and nitrogen give merely the proportions of nitrogen and total paraffin hydrocarbons. The analytical data are sufficient for calculation of the average molecular weight of the paraffin hydrocarbons, or in other words, of the mean value of "n" in the formula C_nH_{2n+2}. Accordingly, if not more than two homologous paraffins are present, the percentage of both individual paraffins can be computed. When the mixture contains more than two paraffin hydrocarbons, the analytical data obtained by combustion methods are inadequate for a complete calculation of the proportion of each individual paraffin.[15]

Explosion methods of analysis consist essentially of the ignition of a portion of the residual gas with a measured excess of air in a glass explosion chamber by a high-tension electric spark passing between two electrodes. The explosion is generally effected under reduced pressure and the electrodes are usually of platinum, fused into the glass chamber. From the diminution of volume which occurs and the amount of carbon dioxide produced, the composition of the initial gas mixture can be calculated. After the explosion the volume of gas is remeasured. The carbon dioxide and excess oxygen are then determined by absorption in potassium hydroxide and alkaline pyrogallol solutions, respectively. The residual gas consists of the nitrogen in the original sample together with that of the added air.

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[10] *Fuel*, 1924, **3**, 246; *Chem. Abs.*, 1924, **18**, 3296; MacGillivray (*J.C.S.*, 1932, 944) recommended dilution of the gas with 8 times its volume of oxygen before treatment with palladium at 80°-90° C.

[11] *Z. physik. Chem. Unterricht*, 1926, **39**, 121; *Chem. Abs.*, 1928, **22**, 2302.

[12] *Ber.*, 1910, **43**, 243.

[13] *Fuel*, 1928, **7**, 45; *Chem. Abs.*, 1928, **22**, 2123.

[14] *Fuel*, 1929, **8**, 560; *Brit. Chem. Abs.* **B**, 1930, 90.

[15] Three hydrocarbons in a mixture (C_aH_b, C_cH_d, and C_eH_f) can be determined by combustion methods provided that ad + be + cf is not equal to af + bc + de; see Kobe, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 262.

If A = volume[16] of hydrocarbon and nitrogen mixture
B = volume of air added
C = contraction in volume after explosion
D = volume of CO_2 produced
E = volume of residual oxygen
F = volume of residual gas (nitrogen)
n = number of carbon atoms in the paraffin hydrocarbon (C_nH_{2n+2}) or average number in the mixture.

then[17]

$$(1)\quad \frac{\text{Carbon dioxide}}{\text{Contraction}} = \frac{D}{C} = \frac{2n}{n+3}$$

and

$$(2)\quad \frac{\text{Carbon dioxide}}{\text{Oxygen used}} = \frac{D}{0.206B - E} = \frac{2n}{3n+1}$$

From both of these equations the average value of "n" can be calculated. Provided the explosion had been carried out satisfactorily and that only paraffin hydrocarbons were present, these two values should agree. Values of "n" calculated by equation (1) are usually somewhat more accurate than those obtained by equation (2).[17]

The actual amount of total paraffin hydrocarbons can be readily deduced, since

$$(3)\quad \text{Volume of paraffins} = \frac{CO_2\text{ produced}}{\text{Mean "}n\text{"}} = \frac{D}{n}$$

This calculation may be checked by the following equation:

$$(4)\quad \text{Volume of total paraffins} = \text{initial volume} - \text{residual nitrogen} = A - F + 0.794\,B$$

From the proportion of total paraffins in the gas mixture and the mean value of "n," the proportion of each constituent can be readily calculated, provided that not more than two homologues were present.

The practical details of the explosion procedure are described in various manuals[18] but a few of the obvious difficulties may be mentioned. The proportion of air necessary for complete combustion of gases of unknown composition is often difficult to determine. A too violent explosion must be avoided since it tends to promote the formation of oxides of nitrogen and the deposition of carbon. Instead of air, mixtures of air and oxygen may be used. If the proportion of oxygen in such mixtures becomes too high, there is a definite risk of contamination by the products of combustion of grease on the walls of the explosion vessel and stopcocks.[19] In the explosion of homologues of methane the difficulties are somewhat enhanced by the considerably greater quantity of oxygen required. For accurate explosion analyses, a sufficient excess of air or oxygen should be added to provide for complete combustion and to prevent too violent an explosion. When in doubt, a considerable excess of air or air-oxygen mixture should be employed. Should the mixture prove to be non-explosive on passing a spark, it can easily be made flammable by the addition of a small amount of electrolytic gas (a mixture of 2 volumes of hydrogen and 1 volume of oxygen). Although the explosion method is quite satisfactory for gas mixtures containing methane and ethane, its application to those having a large content of higher paraffins is attended with difficulty.

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[16] These "volumes" can be expressed in volume units at constant pressure or (as in analysis on the Bone and Wheeler apparatus) in pressure units (mm. of mercury) at constant volume.

[17] These equations apply only when air (O_2 = 20.6%) is used as the oxidizing agent. When oxygen or air-oxygen mixtures are used, the numerical factors in equations (2) and (4) are altered correspondingly.

[18] See, for example, White, "Technical Gas and Fuel Analysis," McGraw-Hill Book Co., Inc., New York, 1913, 41; Dennis, "Gas Analysis," Macmillan Co., New York; Gill, in Scott's "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, 1917, 703.

[19] However, MacGillivray (*J.C.S.*, 1932, 941) states that pure oxygen may be employed for the explosion analysis of methane-ethane mixtures provided appropriate precautions are taken.

Another method of conducting the complete oxidation of gas mixtures containing nitrogen and paraffin hydrocarbons consists in repeatedly passing the mixture together with a very large excess of air or air-oxygen mixture over a heated platinum spiral. This method is particularly applicable to the determination of methane in relatively small concentrations (for example, the air of coal mines).[20]

For the complete combustion of gas mixtures containing appreciable proportions of higher paraffins, passing the mixture over hot copper oxide has been found satisfactory. However, this method is not quite quantitative but for most purposes it furnishes results of sufficient accuracy. The copper oxide appears to retain some of the carbon dioxide produced but this may be removed by washing out the hot copper oxide with a stream of air or oxygen-containing gas. The method is superior to explosion procedures in that it avoids the necessity of determining satisfactory proportions of air for complete combustion. The activity of copper oxide in oxidizing gaseous hydrocarbons by this method may be increased by the addition of lead chromate and cobalt oxide.[21]

By complete oxidation in the presence of hot copper oxide, the hydrocarbons are completely converted into carbon dioxide and water. The resulting gas mixture can be withdrawn from the copper oxide by evacuation. During the evacuation, however, small quantities of oxygen, which result from the thermal dissociation of copper oxide, are removed with the gases. The carbon dioxide and oxygen in the mixture can be determined by absorption, the gas remaining after this procedure being nitrogen.

Krogh [21a] determined butane in a gas mixture by the rate of flame propagation. Baxter and Beckham [21b] suggested a diffusion method to be used in conjunction with combustion analysis. The hydrocarbon mixture is allowed to diffuse into the air for a definite time, a sample is then withdrawn from the remaining mixture and this, as well as a sample of the original gas, is subjected to combustion. From the results of the two combustions the percentage composition of the gas can be calculated.

ANALYSIS BY CONDENSATION

As previously pointed out, the usual absorption and combustion analyses are in themselves quite inadequate for a complete analysis of natural gases, gases from cracking plants and hydrogenation units and similar complex hydrocarbon gas mixtures. To analyze such mixtures completely it becomes necessary to subject them to some type of physical separation, for example, to low-temperature condensation and fractional distillation of the liquefied mixture. The first efforts to apply low-temperature technique to the analysis of gaseous hydrocarbon mixtures involved a series of fractional condensations at low pressures in a series of bulbs maintained at several appropriate low temperatures. Later developments, however, demonstrated the superiority of methods of fractional distillation over those of fractional condensation.

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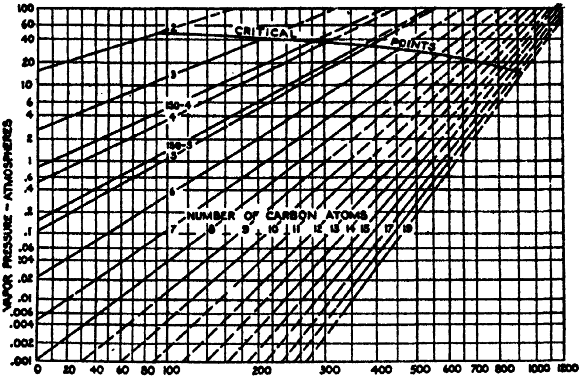
[20] See Jones, *U. S. Bur. Mines. Rep.* 299-B-70, 1922. Ambler (*Analyst,* 1931, 56, 635; *Brit. Chem. Abs.* A, 1931, 1391) determines small amounts of methane in a gas mixture by oxidizing the hydrogen and carbon monoxide with copper oxide at 300° C. and absorbing the water and carbon dioxide in calcium chloride and "ascarite." The methane is then determined by combustion in the presence of platinum.

[21] Campbell and Gray, *J.S.C.I.*. 1930, 49, 432T, 447T, 450T; *Chem. Abs.*, 1931, 25, 473.

[21a] *Petroleum Eng.*, 1930, 1 (13), 111; *Chem. Abs.*, 1930, 24, 5464.

[21b] *J.A.C.S.*, 1933, 55, 3926.

The analytical separation of any individual hydrocarbon from a mixture of homologous hydrocarbons by fractionation becomes more difficult as the series is ascended. This fact becomes obvious from a study of the variation in vapor pressure of the homologous hydrocarbons with temperature[21c] (see Figs. 34 and 35). As the series is ascended the individual vapor pressures tend to approach one another more closely, whereas great differences exist between the vapor pressures of the first few members of the series. The difficulties associated with the fundamental analysis of hydrocarbon mixtures are thus quite obvious.[22] Fortunately, there are only about twenty known gaseous hydrocarbons whose boiling points at atmospheric pressure are within a range of 170° C., and only a rare mixture would probably contain them all.



Courtesy Industrial and Engineering Chemistry

FIG. 34.—Vapor Pressures of Paraffin Hydrocarbons.
(Maxwell.)

Ramsey and Travers[23] separated and analyzed nitrogen, oxygen, helium, argon and other rare gases of the atmosphere by condensation and distillation at low temperatures. The principles of this method later found application in hydrocarbon gas analysis. Stoltzenberg[24] and Erdman and Stoltzenberg[25] developed an apparatus for investigation of gas mixtures such as ethylene and hydrogen, ethylene and oxygen, or carbon dioxide and oxygen. The gas was passed through baths maintained at such a temperature that one of the constituents was condensed while the other was collected in a eudiometer. Lebeau and Damiens[26] employed Ramsey and Travers' method, that is, they maintained the gas mixture at a temperature at which the vapor pressure of one or more of its components is inappreciable and withdrew the others. They separated the individual gases in pairs and

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[21c] These figures were prepared by Maxwell (*Ind. Eng. Chem.*, 1932, 24, 502) and Davis (*ibid.*, *Anal. Ed.*, 1929, 1, 62), respectively.

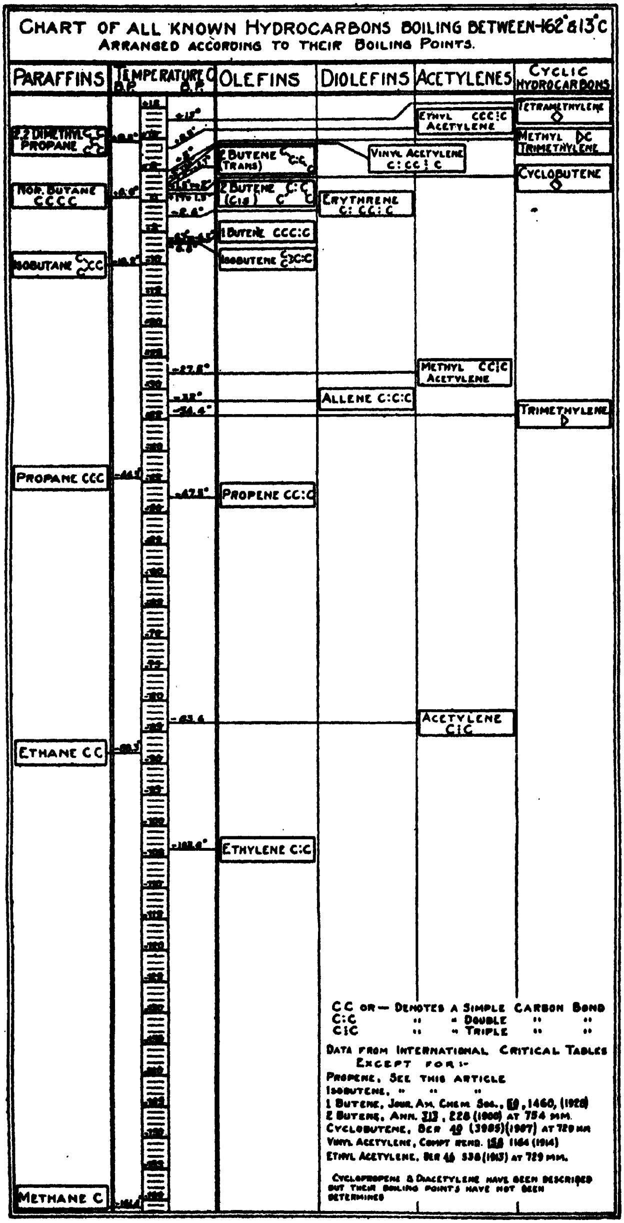
[22] *Cf.* Davis, *Ind. Eng. Chem.*, *Anal. Ed.*, 1929, 1, 61; Podbielniak, *ibid.*, 1933, 5, 135.

[23] Travers, "The Experimental Study of Gases," Macmillan and Co., Ltd., London, 1901.

[24] *Ber.*, 1910, 43, 1708.

[25] *Ber.*, 1910, 43, 1702.

[26] *Compt. rend.*, 1913, 156, 325; *Chem. Abs.*, 1913, 7, 1338.



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 35.

made no mention of the necessity of refractionating to obtain pure constituents. However, they designated the temperatures at which pairs of paraffin and olefin gaseous hydrocarbons could be separated.

Burrell, Seibert, and Robertson,[27] who described the application of low-temperature methods to the analysis of natural gas, employed a procedure based on simple distillation of the liquefied hydrocarbon mixture at low temperatures and pressures. The manipulation was tedious and time-consuming and many series of simple distillations were necessary to separate the individual hydrocarbons. The gas sample was liquefied at the temperature of liquid air and the uncondensed portion and most of the methane were removed by means of a Töpler pump. The residue was vaporized and again liquefied at liquid-air temperature and more methane pumped off. This sequence of operations was repeated until no methane was extracted and the system was under high vacuum. At the temperature of liquid air, ethane and higher paraffins possess a negligible vapor pressure so that it is possible to separate completely the methane and uncondensible gases from other paraffin hydrocarbons.[28] The separation of homologues of methane by this simple distillation process is much more difficult and requires many redistillations. Burrell and his collaborators accomplished the separation of ethane from propane by a series of low-pressure distillations at —153° C. to —140° C. and propane was separated from butanes and higher homologues by a similar procedure at —135° C. to —120° C. The residual liquid, consisting of butanes and higher hydrocarbons, was then vaporized, pumped away, and its volume was measured.

An apparatus, developed by Shepherd and Porter,[29] employs the same principle as that used by Burrell. It was designed to shorten the number of manipulations and the time necessary for analysis. In this apparatus no column is used, the fractionation being insufficient to separate butanes from pentanes or to determine the individual isomers, isobutane and isopentane. The apparatus and procedure are complex, so that it has only been employed for special research purposes. The application of this apparatus to the determination of the gasoline content of natural gas has been described by Shepherd.[30] A modification of the Shepherd-Porter apparatus was employed by Frey and Yant[31] for the analysis of gases from low-temperature carbonization of coal. Fractions obtained from a sample using the Shepherd apparatus were further analyzed by absorption and combustion methods. Frey and Yant[32] introduced an addition to the Shepherd apparatus, a fractionating column for the further separation of the butanes and heavier fractions.

Methods of analysis of mixtures of gaseous hydrocarbons of two or more carbon atoms, which do not involve the use of an efficient fractionating column, appear to be accurate only when complicated apparatus and lengthy procedures are employed. For the separation of methane and uncondensible gases from higher hydrocarbons, the simple distillation method under high vacuum at the temperature of liquid air is reliable since ethane and higher hydrocarbons have inappreciable vapor pressures under such conditions. With ethane and its homologues, however, it becomes increasingly difficult, if not impossible, to effect com-

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[27] *U. S. Bur. Mines Tech. Paper* 104, 1915; *Chem. Abs.*, 1916, 10, 266. Burrell, Seibert, and Jones, Sampling and Examination of Mine Gases and Natural Gas, *U. S. Bureau of Mines Bull.* 197, 1926.

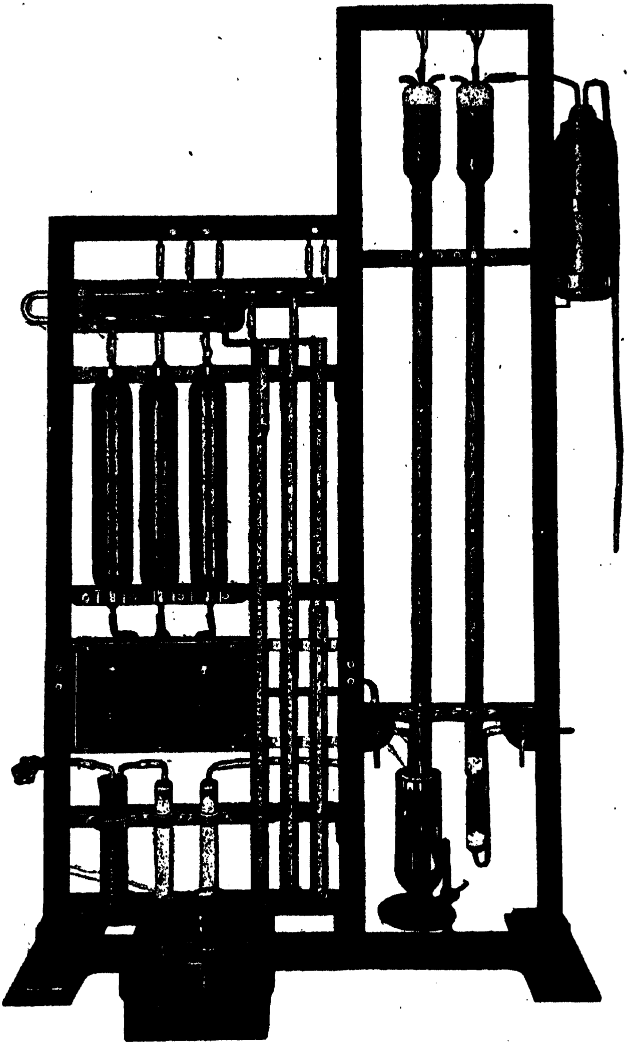
[28] Since ethylene has a considerably greater vapor pressure than ethane, its complete separation from methane by this simple distillation method can hardly be as complete as that of ethane.

[29] *Ind. Eng. Chem.*, 1923, 15, 1143.

[30] *Bur. Standards J. Research*, 1929, 2, 1145; *Chem. Abs.*, 1929, 23, 4562.

[31] *Ind. Eng. Chem.*, 1927, 19, 488; *ibid.*, 1927, 19, 21.

[32] *Ind. Eng. Chem.*, 1927, 19, 492.

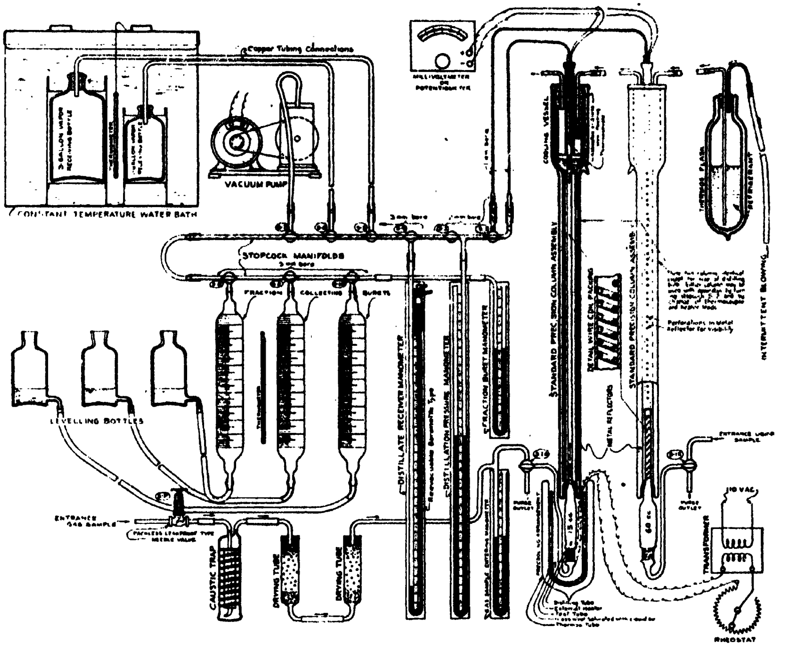


Courtesy Walter J. Podbielniak

FIG. 36.—Podbielniak Standard Precision Apparatus for low-temperature fractional-distillation analysis.

plete separation by such simple procedures since the vapor pressures of these hydrocarbons at any temperature approach one another, as has been mentioned. It is not possible to choose a temperature at which one hydrocarbon has an appreciable vapor pressure while that of its immediate lower homologue is negligible. The separation of methane and uncondensible gases from gaseous hydrocarbons of two or more carbon atoms by simple distillation at liquid-air temperature at low pressures has been described by a number of investigators.[33]

For the analysis of complex hydrocarbon mixtures, Tropsch and Dittrich[34] employed low-temperature fractional condensation to yield a number of fractions, each of which contained not more than two paraffin hydrocarbons associated with the corresponding olefins. The fractions thus obtained were further analyzed by absorption and combustion methods and, since not more than two homologous paraffins were present in each fraction, a complete analysis was possible. This method of fractional condensation thus differs essentially from that of Lebeau and Damiens,[35] Wellers,[36] and Burrell and his collaborators,[37] who used slow distillation under high vacuum. In the method of Tropsch and Dittrich, all the condensible hydrocarbons are liquefied at liquid-air temperature and the uncondensible gas, together with most of the methane, is withdrawn by a Töpler pump. The last traces of methane are removed from the liquefied hydrocarbon mixture by repeated vaporization and condensation followed by evacuation at liquid-air temperature. The gaseous fraction obtained in this way consists of uncondensible gas (nitrogen and hydrogen) and methane. The residual liquefied hydrocarbons



Courtesy Walter J. Podbielniak

FIG. 36a.—Diagram of Podbielniak Standard Precision Apparatus.

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[33] Mulders and Scheffer, *Rec. trav. chim.*, 1930, 49, 1057; *Chem. Abs.*, 1931, 25, 896; Walker and Shukla, *J.C.S.*, 1931, 368; *Chem. Abs.*, 1931, 25, 2077; MacGillivray, *J.C.S.*, 1932, 941.

[34] *Brennstoff-Chem.*, 1925, 6, 169; *Chem. Abs.*, 1925, 19, 2793. *Cf.* Dittrich, *Gas. u. Wasserfach*, 1932, 75, 849; *Brit. Chem. Abs.* B, 1933, 137.

[35] *Loc. cit.*

[36] *Stahl und Eisen*, 1922, 42, 1449; *Chem. Abs.*, 1923, 17, 946.

[37] *Loc. cit.*

are vaporized in a bulb and the gas is passed slowly into a series of three bulbs under high vacuum, each receiver being maintained at a temperature lower than that of the preceding bulb. The bulbs are maintained successively at temperatures of —90° C., —120° C., and at that of liquid air. Tropsch and Dittrich asserted that a partial concentration of the hydrocarbon constituents is thus effected. The bulb maintained at about —90° C. contains paraffins and olefins of four or more carbon atoms, that at —120° C. contains only paraffins and olefins of three and four carbon atoms (i.e., a mixture of propane, butanes, propylene and butylenes) and that cooled to liquid-air temperature contains a mixture of ethane, propane, ethylene and propylene. The last two fractions are vaporized, pumped off, and analyzed separately by absorption and combustion. The liquid volume of the condensate in the bulb at —90° C. may be measured directly.

Undoubtedly some degree of separation may be effected by the procedure of Tropsch and Dittrich, but it is rather doubtful whether this is sufficient for accurate analyses. Because of the marked difference between their vapor pressures, methane and uncondensible gases may be readily separated from higher hydrocarbons by this simple procedure. A great disadvantage of methods of analysis such as that advanced by Tropsch and Dittrich is the necessity of subjecting the fractions to further analysis so that considerable time is consumed.[38]

Low-Temperature Fractionation Methods

The development of efficient fractionating columns and experimental technique has made possible the analysis of complex gaseous hydrocarbon mixtures by fractionation of liquefied gases at low temperatures. The success attained in this direction is largely due to the work of Podbielniak.[39] His apparatus, which has undergone various improvements,[40] is being widely used in the natural-gas, natural-gasoline, and petroleum refining industries, for research purposes as well as for routine analysis of both gaseous and volatile liquid hydrocarbon mixtures. For this reason the apparatus deserves detailed description.

Podbielniak Apparatus. The Podbielniak apparatus[41] consists essentially of a vacuum-jacketed fractionating column, designed for high efficiency at reflux temperatures below atmospheric, together with an accessory apparatus for introducing gas or liquid samples into the column and for temperature and volume measurement. The main features of the apparatus are represented diagrammatically in Figure 37. Figure 38 shows the design of standard precision columns for low- and high-temperature fractionations which possess considerably increased fractionating efficiency and greater sensitivity than previous columns. Both columns are of separate sleeve-type vacuum-jacket construction supplied with a radiant or dry reflux cooling vessel. A variety of distilling tubes and flasks of different diameters can be used interchangeably with either standard vacuum jacket. The vacuum jacket includes only smooth seals and the distilling tube is completely free from bulking seals or other discontinuities. For the low-temperature column, the distilling tubes range from 2.6 mm. to 4.5 mm. in diameter, and for the high-temperature columns, from 2.6 mm. to 8.0 mm. A larger high-temperature column has also been developed, in which tubes of 8.0 mm. up to 15 mm. are used. Single-wire coils up to 6 mm. in diameter and double-wire coils, flat-strip coils or other special continuous type of packing may

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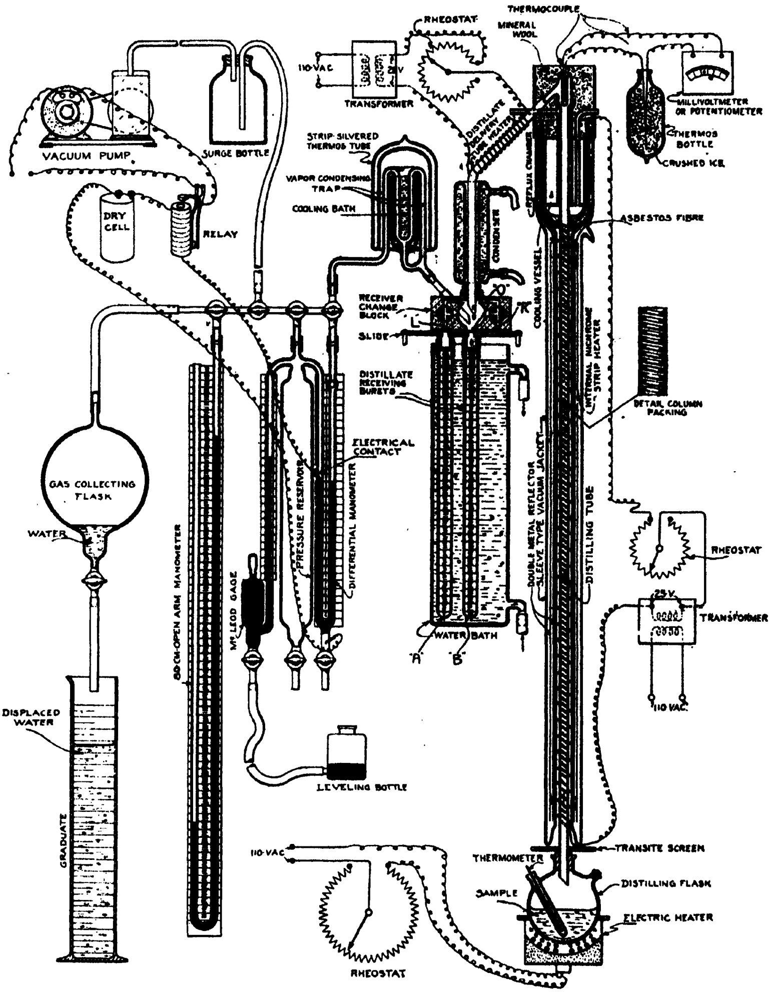
[38] *Cf.* Frey and Yant, *Ind. Eng. Chem.*, 1927, **19**, 492.

[39] The original apparatus developed by Podbielniak was described by Oberfell and Alden, *Oil and Gas J.*, 1928, **27** (22), 142; *Chem. Abs.*, 1929, **23**, 2282. Various stages of its development and its application to industrial and research problems are discussed by Podbielniak in a series of papers: *Oil and Gas J.*, 1929, **27** (35), 38; *Chem. Abs.*, 1929, **23**, 1745; *Oil and Gas J.*, 1930, **29** (20), 235; *Chem. Abs.*, 1930, **24**, 5992; *Oil and Gas J.*, 1929, **27** (52), 30; *Petroleum World* (*Los Angeles*), 1928, **13** (10), 99, 115; *Refiner*, 1929, **8** (3), 55; *Chem. Abs.*, 1929, **23**, 3128.

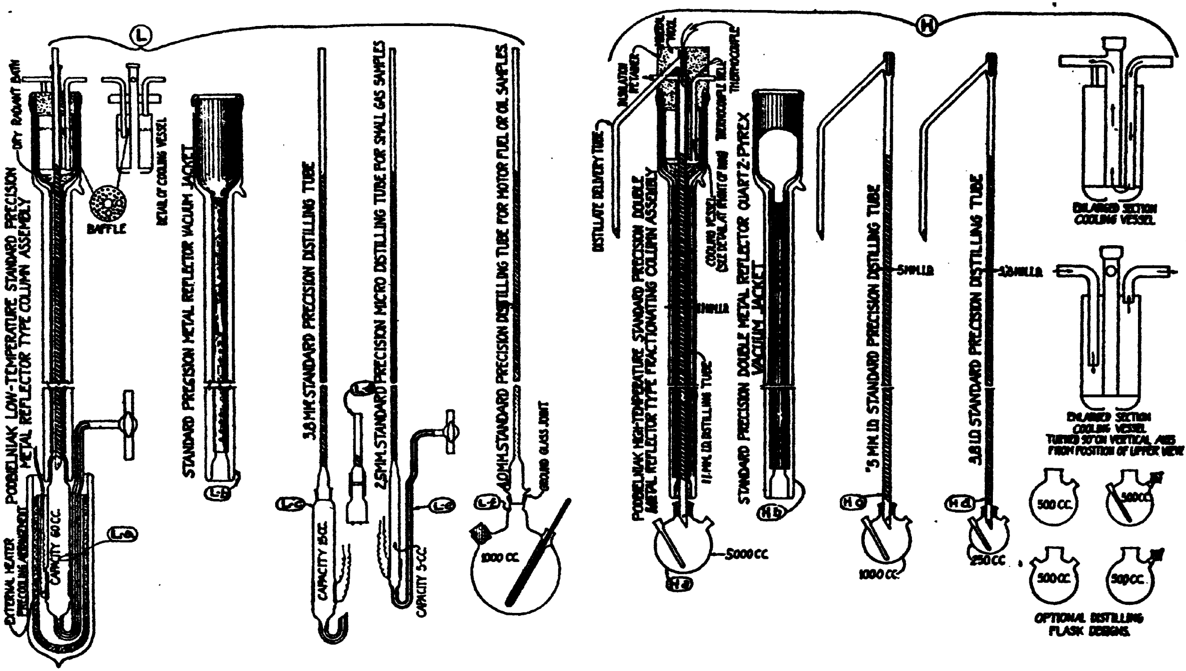
[40] See Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 177.

[41] *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 177; *ibid.*, 1933, **5**, 119, 135; *ibid.*, **5**, 172; U. S. Patent 1,909,315, May 16, 1932; *Chem. Abs.*, 1933, **27**, 3645; U. S. Patent 1,917,272, July 11, 1933; *Chem. Abs.*, 1933, **27**, 4445; U. S. Patent 1,935,888, Nov. 14, 1933; British Patent 380,220, 1932; *Chem. Abs.*, 1933, **27**, 3858; French Patent 721,598, 1931; French Patent 740,353, 1933; *Chem. Abs.*, 1933, **27**, 3858; *Oil and Gas J.*, 1932, **30** (46), 68; *Chem. Abs.*, 1932, **26**, 6111. See Uehara (*J. Chem. Soc. Japan*, 1932, **53**, 910; *Chem. Abs.*, 1933, **27**, 246) for suggested improvements on Podbielniak apparatus for the estimation of lower hydrocarbons. Vandaveer *et al.* (*Am. Gas Assoc. Proc.*, 1931, **13**, 1034; *Chem. Abs.*, 1932, **26**, 4450) give a brief history of the development, manipulation and application of the Podbielniak, Phillips, Shepherd-Porter and Burrell, Robertson and Seibert apparatuses.



Courtesy Walter J. Podbielniak

FIG. 37.—Diagram of Podbielniak High-Temperature Fractional Distillation Apparatus.


L
H
PODBIELNIAK LOW-TEMPERATURE STANDARD PRECISION METAL REFLECTOR TYPE COLUMN ASSEMBLY
DRY RADIANT BATH
EXTERNAL HEATER
PRECOOLING ARRANGEMENT
CAPACITY 60 CC.
L-a
BAFFLE
DETAIL OF COOLING VESSEL
STANDARD PRECISION METAL REFLECTOR VACUUM JACKET
L-b
3.6 MM. STANDARD PRECISION DISTILLING TUBE
CAPACITY 15 CC.
L-c
2.5 MM. STANDARD PRECISION MICRO DISTILLING TUBE FOR SMALL GAS SAMPLES
CAPACITY 5 CC.
L-d
L-e
4.0 MM. STANDARD PRECISION DISTILLING TUBE FOR MOTOR FUEL OR OIL SAMPLES
GROUND GLASS JOINT
1000 CC.
L-f
PODBIELNIAK HIGH-TEMPERATURE STANDARD PRECISION DOUBLE METAL REFLECTOR TYPE FRACTIONATING COLUMN ASSEMBLY
DISTILLATE DELIVERY TUBE
INSULATOR RETAINER
MINERAL WOOL
THERMOCOUPLE WELL
THERMOCOUPLE
COOLING VESSEL (SEE DETAIL AT RIGHT OF H-d)
11 MM. I.D. DISTILLING TUBE
5000 CC
H-a
STANDARD PRECISION DOUBLE METAL REFLECTOR QUARTZ-PYREX VACUUM JACKET
H-b
5 MM. I.D. STANDARD PRECISION DISTILLING TUBE
1000 CC
H-c
3.8 I.D. STANDARD PRECISION DISTILLING TUBE
250 CC
H-d
ENLARGED SECTION COOLING VESSEL
ENLARGED SECTION COOLING VESSEL TURNED 90° ON VERTICAL AXIS FROM POSITION OF UPPER VIEW
500 CC.
500 CC.
OPTIONAL DISTILLING FLASK DESIGNS

Courtesy Walter J. Podbielniak

FIG. 38.—Standard Podbielniak Precision Fractionating Columns. L—Metal reflector low-temperature assembly. H—Metal reflector high-temperature assembly.

be used. It is only necessary with this separate vacuum-jacket distilling tube combination to change the distilling tubes to carry out a small or large capacity determination. The low-temperature column contains a single perforated reflector in the vacuum space of the vacuum jacket. The high-temperature column has a chamber reflector plus a compensatory miniature resistance wire heater inside the jacket inner tube. The low-temperature column depends on initial bowing of the Pyrex inner tube to compensate for differential contraction and the high-temperature column contains a quartz inner tube to withstand extreme temperature ranges. Larger distilling tubes can be used with the high-temperature jacket than with the low-temperature. The dry reflux cooling arrangement is said to be superior to any type of gasoline or other liquid bath. The low-temperature cooling vessel is provided with a soldered-on cap and packing gland to exclude atmospheric moisture which might otherwise condense and freeze in the reflux chamber. The high-temperature cooling vessel has no cap and is brazed to withstand high temperatures. The low-temperature cooling vessel may be used alternatively with refrigerants such as liquid air, liquid carbon dioxide, brine, water, compressed air. The vapor temperature at the head of the column is measured with an accurately calibrated thermocouple connected to a millivoltmeter. The distilling bulb is insulated by a vacuum jacket and to it is supplied a regulated heat input by an external resistance wire arranged as shown in the diagram. The droplets of refluxed liquid falling down the column may be counted by means of a drip indicator with small perforations, which are necessary to avoid flooding of the column. At the bottom of the column is a hairpin precooling tube which may be immersed in a cooling bath when a gaseous or volatile liquid sample is being introduced into the column.

The principle of the operation of the Podbielniak Apparatus is simple, although the practical details and experimental technique are only acquired by practice. Essentially, the process consists in subjecting the liquefied sample to slow fractionation under standard conditions of reflux ratio and withdrawing the vapors continuously at a definite pressure. The vapors pass into a vessel of known volume maintained in a thermostat and changes of the absolute pressure in this container are observed on a manometer. The analytical results are best expressed in the form of a graph in which the pressure readings are plotted against the corresponding temperatures recorded by the thermocouple. The operation of the apparatus may be varied to permit analytical distillation of components of volatility varying from methane to hexanes or heptanes. The distillation of octanes and heavier fractions is not usually practicable in this apparatus. The distillations are generally conducted isobarically at atmospheric pressure, but hydrocarbons of five or more carbon atoms are usually fractionated under diminished pressure. It is important that reflux temperatures never approach atmospheric temperature. The recommended distillation pressures are as follows:

For all compounds of boiling point lower than atmospheric temperature	Atmospheric pressure
Pentanes and pentenes	300 mm. (absolute)
Hexanes and hexenes	100 mm.
Heptanes	20 mm.

As previously indicated, the distillate is usually collected in vapor form in evacuated glass bottles maintained at constant temperature. The amount of distillate is computed from the calibrated volume of the receiver bottle and from the temperature and pressure of the contained vapor, using known physical constants and ideal gas laws. Errors introduced by the deviation of the higher hydrocarbons from the ideal gas laws[42] may be avoided by collecting the hydrocarbons below standard maximum partial pressures as shown in Table 160:

TABLE 160.—*Maximum Partial Pressures in Vapor Receiving Bottle.*

Hydrocarbon	Max. Partial Pressure Mm.
Methane	760
Ethane	760
Propane	760
Butanes	400
Pentanes	80
Hexanes	20
Heptanes	5

The gas to be analyzed is introduced into the evacuated apparatus through the precooling tube attached to the bottom of the distilling bulb. The sample, which should usually be about 6 liters vapor volume, is preferably subjected to total condensation by allowing it to pass slowly into the precooling tube and distilling bulb, both of which are cooled with liquid air. By this procedure, practically all the methane and higher hydrocarbons are condensed. Another method of introducing the gas sample consists in precooling the sample in a bath of gasoline cooled with liquid air. This latter method requires less time, since the bulk of the methane in the sample is discharged from the top of the column simultaneously with the introduction of the gas, instead of being condensed and subsequently distilled off slowly. It is absolutely essential that all water vapor and carbon dioxide be removed from the gas sample prior to its introduction into the apparatus, since these constituents would freeze in the column and consequently obstruct the distillation. The removal of these constituents is effected by passing the gas through a potash trap and a phosphorus pentoxide bulb.[43]

The method of carrying out an analysis is described by Podbielniak as follows: Once a sample is entered into the column, the analytical procedure is essentially the same, whether the sample is natural gas, coal gas, liquefied petroleum gas, natural gasoline, or ordinary motor fuel. The pressure in the column is brought to atmospheric by applying heat to the distilling-bulb heating element (regulating with the transformer shown), or by cooling the reflux with liquid air, depending on whether the column pressure is below or above atmospheric. The vapor formed passes up the column and is condensed at the reflux. In order to maintain this flow of reflux liquid down the column it is necessary to extract heat from the reflux by periodically blowing more liquid air into the reflux cooling vessel. The supply of current to the column-heating element and the cooling of the reflux should be so balanced that (1) the column pressure is practically atmospheric, and (2) the entire wire packing of the column is wet with the minimum amount of reflux to form capillary liquid films.

When the proper conditions have been established in the column, distillation may be commenced by cracking stopcock 4 to allow the fractionated overhead vapor to pass slowly through the stopcock train into the receiving bottle which had been evacuated previously to a fairly low pressure. The barometric manometer connected to the receiving bottle indicates the rise in pressure in this bottle as it fills with vapor. This rate of distillation is controlled by changing the setting of stopcock 4 so as to secure the best possible fractionation compatible with a maximum permissible total time for the distillation. In practice this is equivalent to slowing the distillation rate to a very low value whenever the vapor temperature tends to rise at constant pressure, and increasing the distillation rate when the temperature tends to stay constant. In this way, one hydrocarbon after another is distilled with very sharp temperature rises until the entire sample is distilled or until an undistillable residue remains. Frequent simultaneous readings, (1) of the thermocouple e.m.f.'s indicated by the millivoltmeter, (2) of column pressure on the open-arm manometer, and (3) of the pressure on the receiving-bottle manometer, are taken to enable the operator to construct subsequently a plot of vapor temperature (corrected to a standard pressure) against the amount of vapor distilled.

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[42] Rogers and Brown, *Ind. Eng. Chem.*, 1930, 22, 258.

[43] When unsaturated hydrocarbons are present, phosphorus pentoxide cannot be used as it absorbs these gases. Magnesium perchlorate trihydrate is satisfactory in such cases.

The vapor temperatures at the top of the column are read by the analyst on the millivoltmeter, which is graduated to tenths of a millivolt.

The column-pressure readings on both arms of the open-arm manometer connected to the fractionating column are recorded. When the mercury stands at the same level in both arms, the pressure in the column is atmospheric.

The pressure on the closed arm of the closed-arm manometer connected to the vapor-receiving bottle used in the analysis are recorded as bottle pressure. These readings must be taken with care and estimated to tenths of a millimeter. Each series begins with an initial low pressure in an evacuated vapor-receiving bottle and ends with the maximum permissible pressure in the bottle. After each final reading the bottle is reevacuated and another series of readings taken. This is done as often as required.

Several times during an analysis, readings (correct to 0.1° C.) are taken of the temperature of the water bath in which the vapor-receiving bottles are immersed. These readings should be taken preferably at the break points on the fractional distillation curve, as evidenced by sudden temperature rise. Failure to record these readings may lead to considerable error in analysis, especially when the laboratory temperature fluctuates considerably.

The corrected temperatures are obtained by multiplying the vapor-temperature readings by 10 (the calibration curve of the thermocouple should be used for precise work), and converting to temperatures at atmospheric pressure by means of a chart.

The calculated pressures are obtained from the bottle-pressure readings by the following procedure. The initial reading of the first series in the bottle-pressure column (which is not necessarily zero) is subtracted from itself and then successively from every other reading of the series to yield the corresponding calculated pressures. To convert the second series of bottle-pressure readings, the final calculated pressure of the first series is subtracted from the initial reading of the second series $(0.0 - 94.0 = -94.0)$, and from every other reading of the series in succession. The third and following series are converted similarly. The effect of this procedure is to arrange all the millimeter intervals in the bottle-pressure columns of the tables into one continuous series beginning with zero to be proportional at any point to the total volume (in vapor form) of the sample distilled.

The results so obtained are plotted in graphical form to yield a fractionation curve as shown in Figures 39 and 40. The ideal fractionation curve would consist of perfectly horizontal plateaus and rectangular rises in temperature. The curves actually obtained approximate this ideal quite closely except for hydrocarbons having boiling points not far apart. In order to determine the proper cut points on the temperature rises in the curve, Podbielniak advises the use of a so-called "equal area" method[44] rather than the mid-point method. Each plateau on the curve corresponds to a pure hydrocarbon which can be identified by its boiling point, and the amounts of hydrocarbons are proportional to the lengths of these plateaus. In the analysis of gaseous products with no liquid residue, the gas per cent by volume is readily calculated simply by dividing each plateau length (A mm.) by the sum of the lengths of all the plateaus for the entire sample and multiplying by 100. Liquid per cent by volume for normally liquid hydrocarbons may also be calculated from these curves.

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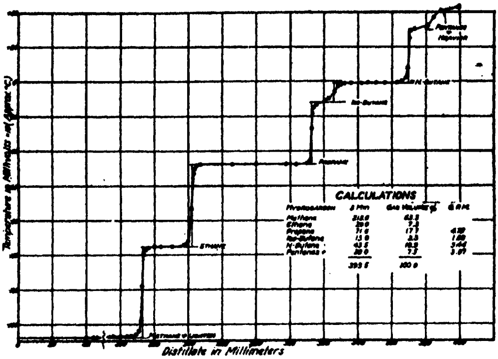
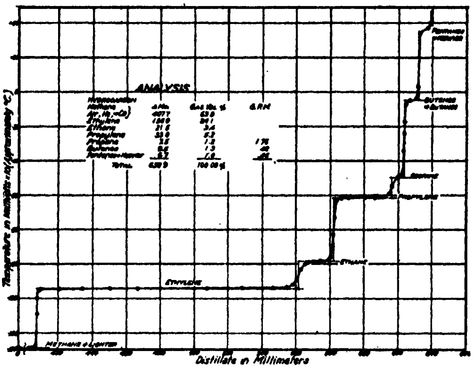
[44] Podbielniak, *Refiner*, 1929, **8** (3), 55; *Chem. Abs.*, 1929, **23**, 3128.

Other Fractionation Columns. Frey and Yant[45] used a column for the fractionation of the four-carbon atom fraction of low-temperature coal carbonization gas, which was of Pyrex glass, 50 cm. high and 9 mm. in diameter filled with 5 mm. brass rings. Controlled reflux was obtained by regulated heat withdrawal from the uppermost 10 cm. of the column. This was effected by cooling with liquid air through a 1 mm. thick annular interspace filled with hydrogen at a regulated pressure. Since the heat transmission through the interspace depends mainly upon the pressure of the hydrogen, the rate of cooling can be controlled merely by adjusting the hydrogen pressure. The fractionating column proper was thermally insulated by means of a vacuum jacket.



Courtesy Walter J. Podbielniak

FIG. 39.—Fractional-Distillation Curve of Natural Gas Obtained in Podbielniak Apparatus.



Courtesy Walter J. Podbielniak

FIG. 40.—Fractional Distillation Curve of Refinery Cracked Gas Obtained in Podbielniak Precision-Type Column.

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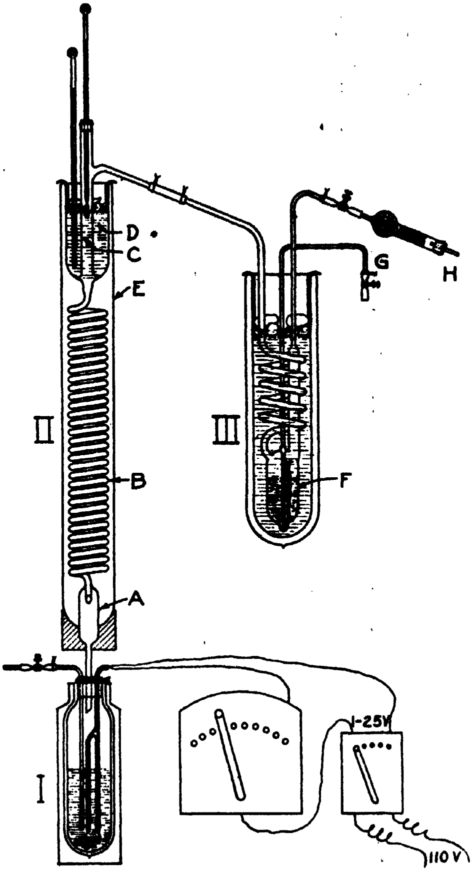
[45] *Loc. cit.*

A simple fractionating column capable of being used for the estimation of various unsaturated hydrocarbons has been described by Davis.[46] This column, represented in Figure 41, consists of 3 to 5 meters of 5 mm. glass tubing bent into a low-pitched spiral of 30 to 40 turns. Thermal insulation and mechanical rigidity is secured by surrounding the column with a glass jacket which is highly evacuated and silvered, unsilvered strips being left on opposite sides for observation. Reflux cooling is obtained by surrounding the upright column head by a glass jacket containing a cooling mixture. Other features of this column, which is not satisfactory for the investigation of gases with boiling points lower than that of ethane, include an immersion-type electrical heating device and a cooled receiver for condensation of distillate vapors.



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 41.—Davis Apparatus for Fractionating Liquefied Gases.

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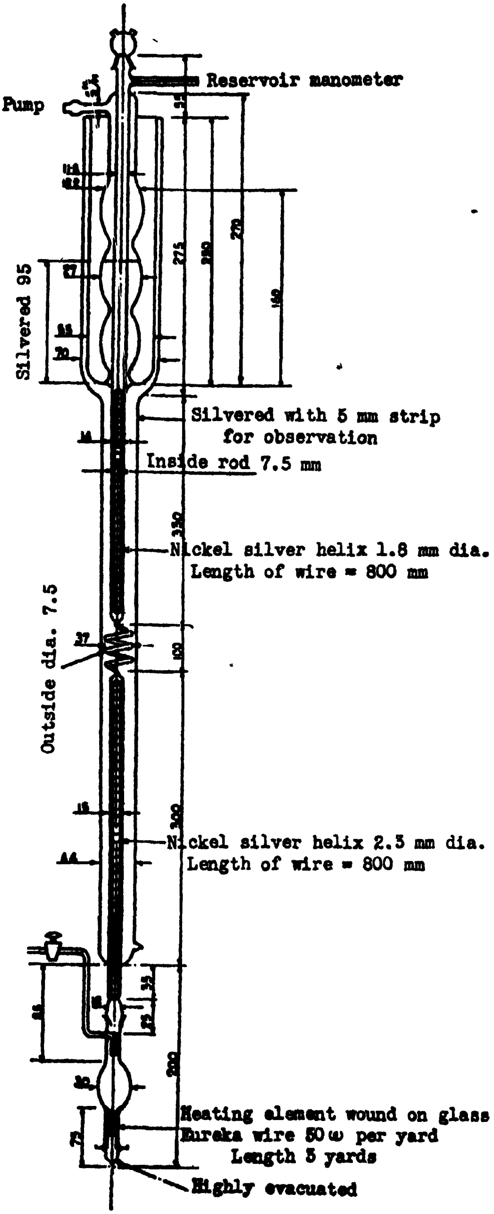
[46] *Ind. Eng. Chem., Anal. Ed.,* 1929, 1, 61. *Cf.* Davis and Daugherty, *Ind. Eng. Chem., Anal. Ed.,* 1932, 4, 193.



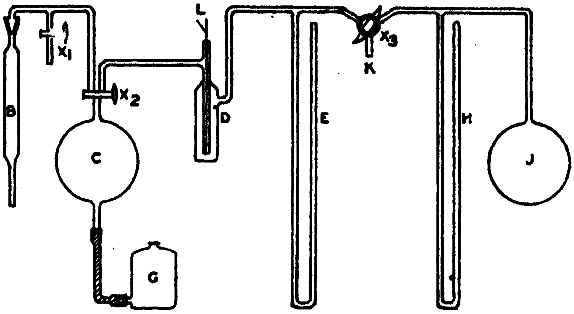
Courtesy Journal of the Chemical Society

FIG. 42.—MacGillivray Fractionating Column.

Schaufelberger[47] described the analysis of hydrocarbon mixtures by fractionation with a column similar to that of Podbielniak. The vacuum-jacketed column (silvered completely except for one window at the drip indicator, which is placed high in the column) is joined by a cork to a separate reflux chamber, which is cooled with a gasoline bath agitated by a turbine-type stirrer.

For the preparation of pure ethane, methane, and hydrogen, MacGillivray[48] used a column similar to that of Podbielniak. The column, which is represented in Figure 42, can be employed for the analysis of complex hydrocarbon mixtures, particularly for the separation of saturated from unsaturated hydrocarbons. In this apparatus the reflux is controlled by a variable-pressure hydrogen buffer. MacGillivray recommended that liquid nitrogen be used as the refrigerating liquid instead of liquid air, for in the event of a break or crack occurring in the apparatus, with consequent mixing of liquid hydrocarbons and liquid air, a dangerous explosion may result.[49]

A short-cut method of analysis of hydrocarbon mixtures, satisfactory for routine control analyses, has been described by Rosen and Robertson.[50] The applicability of this procedure is limited to the analysis of ternary mixtures containing ethane, propane, and butanes and to mixtures of these hydrocarbons containing methane and fixed gases. The extension of the method to more complex mixtures of hydrocarbons is indicated, however. With a ternary mixture such as that mentioned, the analysis is said to be reliable to 0.5 per cent on any constituent. The essential principles of the method are as follows: The liquefied hydrocarbon mixture is first freed from fixed gas and methane by evacuation at the temperature of liquid nitrogen, and the resulting liquid is submitted to distillation into a receiver of known volume connected to a mercury manometer. The temperature of the liquid hydrocarbon mixture is measured with a thermocouple junction which passes to the bottom of the condensation bulb and so records liquid temperature. Distillations are conducted at 760 mm. pressure and at a fairly constant rate of about 15 cc. of gas per minute. During the distillation, simultaneous readings on the thermocouple potentiometer and on the manometer are taken as the voltage changes 0.1 to 0.2 millivolt, or as the



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 43.—Rosen and Robertson Fractionating Apparatus.

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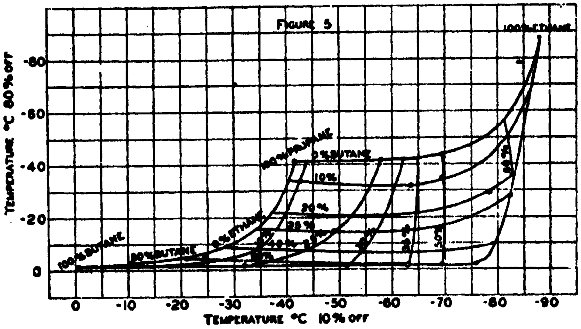
[47] *Oil and Gas J.*, 1930, **29** (16), 46; *Chem. Abs.*, 1930, **24**, 5995.

[48] *J.C.S.*, 1932, 941.

[49] A fatal explosion of air and light petroleum was experienced at the U. S. Bureau of Standards on Sept. 20, 1923 (see *Chem. Met. Eng.*, 1923, **29**, 639; *Chem. Abs.*, 1923, **17**, 3790).

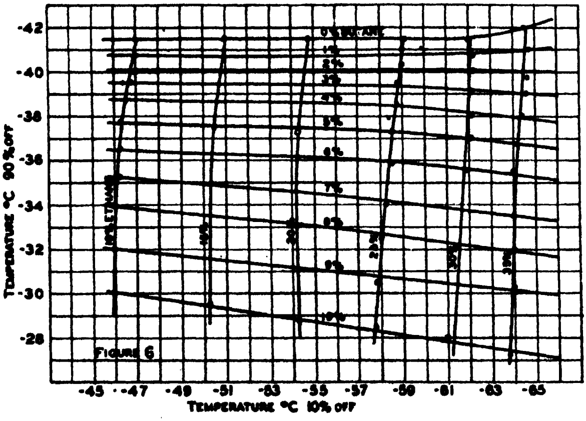
[50] *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 284; *ibid.*, 1934, **6**, 12.

pressure rises 5 to 10 mm. Heat input to the still is controlled by lowering a Dewar flask placed round a cooled aluminum cylinder (which is fitted snugly round the distilling bulb), thus increasing the surface of the aluminum cylinder exposed to room temperature. A simple apparatus for conducting this process is shown in Figure 43, in which C is the vessel for measuring the gas sample,[51]



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 44.—Master Graph for Mixtures of Ethane, Propane and Butane. (Rosen and Robertson.)



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 45.—Enlarged Section of Master Graph, for Mixtures of Ethane, Propane and Butane. (Rosen and Robertson.)

D is the condensation vessel and still, and J is the receiver of known volume, connected to the manometer H. The rate of distillation is controlled by stopcock X_3 and the distillation pressure is recorded on manometer E. It will be noticed that no fractionating column is employed, the operation being merely one of simple distillation. Any methane or condensible gas in the sample is removed by a mercury vapor pump K. When the distillation is completed, stopcock X_3 is opened and the total pressure, P_2, on the manometer H is noted. From the barometric pressure, the volumes of the measuring flask and expansion bulb, the pressure P_1, corresponding to the volume of the sample taken, is calculated by the formula:

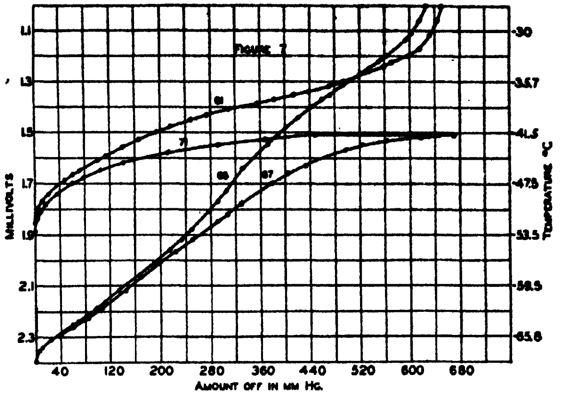
---

[51] The gas sample must be freed from carbon dioxide, hydrogen sulphide and water vapor before introduction into C.

$$P_1 = \frac{\text{volume of sample} \times \text{atmospheric pressure}}{\text{volume of (distillation bulb + lines + expansion bulb)}}$$

The difference between P_1 and P_2 represents the pressure due to methane and fixed gases pumped away prior to the distillation, and $\frac{(P_1 - P_2)\,100}{P_1}$ = Percentage of fixed gases and methane in the sample analyzed.

The method of computing the composition of the mixture of ethane, propane, and butanes distilled is as follows: By plotting the temperature recorded on the potentiometer against the receiver pressure in mm., a curve is obtained from which the temperature corresponding to any percentage distilled off may be read. The results are then compared with a master graph showing all possible compositions of the three hydrocarbons. An outline of the master graph is shown in Figure 44 and Figure 45 and gives a section of this in detail. Several typical distillation curves are shown in Figure 46. The temperatures at which, for example, 10 per cent and 80 per cent of the mixture is distilled off at 760 mm. pressure are read from the analytical distillation curve and then, by referring these temperatures to a master chart, the composition of the original sample may be calculated.



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 46.—Typical Distillation Curves obtained with Rosen and Robertson Apparatus.

OTHER PHYSICAL METHODS FOR THE ANALYTICAL SEPARATION OF HYDROCARBON MIXTURES

Several methods of analytical rectification of hydrocarbon mixtures, depending upon adsorption and solution effects, have been advanced. Kuhn[82] described a method of analysis of coal gas or natural gas in which the dried gas is first cooled under reduced pressure to liquid air temperature to condense carbon dioxide and hydrocarbons higher than methane. The uncondensed gases are then subjected to adsorption in silica gel cooled to the temperature of liquid air, which removes methane, carbon monoxide, oxygen and nitrogen, leaving a residual gas composed almost entirely of hydrogen with a little oxygen. The gases condensed in the first liquid air cooler are then separated by fractional distillation at 0.1 mm. pressure, ethane and ethylene being removed at —150° C., acetylene, propane, propylene, and carbon dioxide at about —120° C., and butane, pentane and benzene at —25° C.

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[82] *Z. angew Chem.*, 1931, 44, 757; *Chem. Abs.*, 1931, 25, 5875. *Cf.* Coppens, *Bull. soc. chim. Belg.*, 1932, 41, 525; *Chem. Abs.*, 1933, 27, 2075; Horstmann and Scheffer, *Rec. trav. chim.*, 1932, 51, 143, 153; *Chem. Abs.*, 1932, 26, 1873.

A method of analytical rectification of hydrocarbon mixtures which depends upon the selective solvent action of toluene or toluene-nitrobenzene mixtures on various gaseous hydrocarbons has been described by van Dyck.[58] This method is said to be satisfactory for the determination of pentane, butane and propane in hydrocarbon gas mixtures. With a fractionating apparatus, the various gases are removed from the mixture in the order of their solubilities, starting with the most soluble. The analysis is effected by scrubbing a known volume of gas with a stream of liquid hydrocarbon, fed into the top of the apparatus (Fig. 47) at a definite rate. Solution of some of the gas takes place and the liquid hydrocarbon descends into a spiral column which is heated by vapors of a boiling liquid. A greater part of the dissolved gas is accordingly expelled in this heated spiral so that there is established a gas phase flowing countercurrent to a liquid stream, thus effecting fractionation. The efflux rate of the liquid solvent from the spiral heater is maintained at a steady value during analyses. A great advantage of this type of apparatus is that no liquid air or nitrogen is required, only water cooling and electrical heating being used. The results are said to be accurate to within 0.5 per cent, though the minimum quantity of any component which can be identified with certainty is about 2.5 per cent. The absorption is conducted at constant temperature in a regulated slow stream of liquid solvent, the amount of gas absorbed being measured by volume changes at constant pressure. Analytical results are calculated from graphs obtained by plotting the volume of absorption liquid passed at definite stages of the analysis against the corresponding volume of gas absorbed.

Inverted fractional-distillation analysis, which permits separation of gases or liquids beginning with the components with the highest boiling point has been described by Bosschart.[58a] The apparatus designed for this purpose has a range from +200° C. to —170° C. and the fractions can be collected as liquids or gases. As in the van Dyck absorption method, the reflux is a gas instead of a liquid phase. This type of analysis is especially recommended where the principal interest is in the heaviest components rather than in the light fractions.

DETERMINATION OF UNSATURATED HYDROCARBONS IN GAS MIXTURES

The quantitative estimation of unsaturated hydrocarbons in mixtures is attended with considerable difficulty and can only be accomplished in one or two cases without using some method of fractionation, either of the hydrocarbons themselves or of their derivatives (e.g., of their dibromides). Much work has been reported on methods of analysis of olefin mixtures by absorption in various concentrations of sulphuric acid, with or without the addition of certain metallic salts. With sulphuric acid of appropriate concentration it is undoubtedly possible

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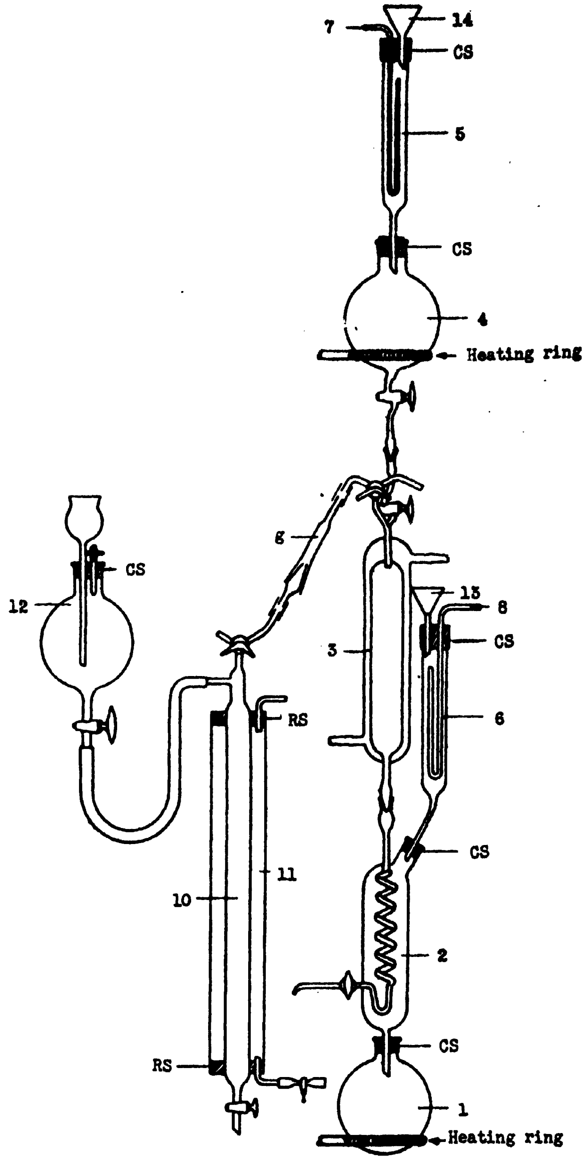
[58] *J. Inst. Pet. Tech.*, 1932, **18**, 145; *Brit. Chem. Abs.* **B**, 1932, 790.

[58a] *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 29.



Courtesy Journal of the Institution of Petroleum Technologists

FIG. 47.—Van Dyck Apparatus for Gas Analysis.

to effect an analytical separation of ethylene, which is absorbed with the most difficulty by sulphuric acid, from its higher homologues. However, the rates of absorption of propylene and the two straight-chain butylenes approach one another so closely that any analytical separation of them by sulphuric acid is apparently out of the question.

The problem of the estimation of the total unsaturated hydrocarbon content of gaseous mixtures is in reality identical with that of the complete absorption of the ethylene from the gas. Ethylene is only completely absorbed with difficulty, whereas the complete absorption of other unsaturated hydrocarbon gases is a relatively simple matter. Bromine water and fuming sulphuric acid are the reagents usually employed for this purpose. Of the two, bromine water is the better, especially if the absorption is carried out in a darkened pipette. Fuming sulphuric acid rapidly absorbs all unsaturated hydrocarbons, including ethylene, but unfortunately it also absorbs paraffin hydrocarbons.[54]

According to Tropsch and Dittrich,[55] the addition of vanadic acid or of uranyl sulphate to concentrated sulphuric acid renders it a satisfactory absorbent for ethylene (and thus for the total unsaturated content) in gases. Even better is a mixture of 15 parts of a 0.6 per cent solution of silver sulphate in 87 per cent sulphuric acid with 2 parts of a saturated solution of nickelous sulphate in 87 per cent sulphuric acid. This solution is said to absorb ethylene readily but not saturated hydrocarbons.[56]

ABSORPTION OF OLEFINS BY SULPHURIC ACID OF VARIOUS CONCENTRATIONS

A number of methods have been proposed for the preferential absorption of various individual olefins by successive treatments with sulphuric acid of increasing concentrations. Tropsch and von Philippovich[57] developed a method of estimating propylene and its homologues in the presence of ethylene by absorption in 87 per cent sulphuric acid. This concentration of acid exerts but slight absorptive effect on ethylene but rapidly absorbs its homologues. However, when large concentrations of ethylene are present in the gas, the results are subject to greater error, since under these conditions the absorption of the ethylene becomes appreciable. The residual ethylene, after absorption of the homologues, can be absorbed in bromine water. Tropsch and von Philippovich stated that the relative rates of absorption of ethylene and propylene in 87 per cent sulphuric acid are as 1 to 100. According to Suida and Wesely,[58] the analytical separation of ethylene from its homologues can be successfully accomplished by absorption of the latter in 87 per cent sulphuric acid, provided the gas mixture does not contain more than 25 per cent of total olefins. The determination of the total olefin content is stated by them to be carried out best by using 0.04 per cent bromine water.

Tropsch and Dittrich[59] subjected the complex hydrocarbon gas mixture to a fractional condensation under such conditions that each fraction contained only two homologous olefins (admixed with the corresponding paraffins). For the absorption of ethylene homologues, these investigators employed 87 per cent sulphuric acid and subsequently absorbed the ethylene in 87 per cent sulphuric acid activated with silver and nickel sulphates. To estimate the relative proportions of the two unsaturated hydrocarbons (higher than ethylene) absorbed from each fraction by 87 per cent sulphuric acid, the solution of these olefins in that acid was oxidized with an excess of potassium iodate. The amount of potassium iodate over that required for oxidation was determined by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate solution.

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[54] For example, Davis and Quiggle (*Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 39) showed that during the absorption of olefins with fuming sulphuric acid (30% SO_3), as much as 3 per cent of n-butane in the mixture was also absorbed.

[55] *Brennstoff-Chem.*, 1925, 6, 169; *Chem. Abs.*, 1925, 19, 2793.

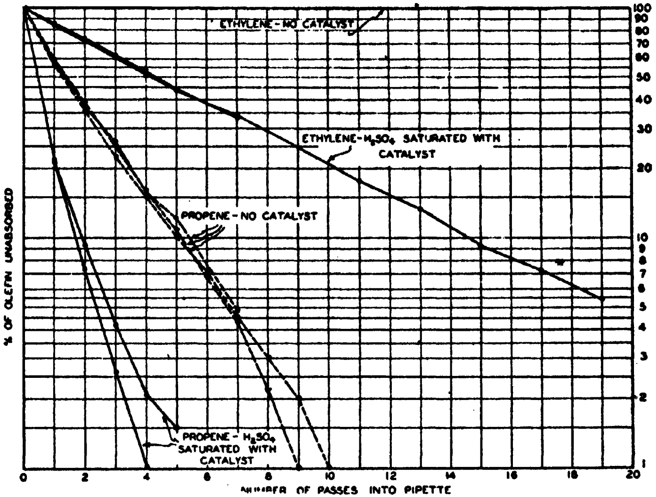
[56] *Cf.* Davis and Quiggle, *Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 39.

[57] *Brennstoff-Chem.*, 1923, 4, 147; *Chem. Abs.*, 1923, 17, 3598.

[58] *Z. anal. Chem.*, 1924, 64, 143; *Chem. Abs.*, 1924, 18, 2858.

[59] *Brennstoff-Chem.*, 1925, 6, 169; *Chem. Abs.*, 1925, 19, 2793.

From a study of the rates of absorption of ethylene, propylene, and isobutylene in various concentrations of sulphuric acid, Dobrjanski[60] developed a method of determining the proportions of these gases in mixtures by bringing the gas successively into contact with (1) 63 to 64 per cent acid, which absorbs only the isobutylene; (2) 83 to 84 per cent acid to absorb propylene;[61] and (3) 100 to 200 per cent acid to absorb ethylene. In a modified procedure for use in the presence of butadiene, isobutylene is absorbed in 45 to 46 per cent acid, propylene and butadiene in 83 per cent acid, and ethylene in dilute fuming sulphuric acid (2% SO_3). A separate sample of the gas is then subjected to a bromine addition estimation by the bromide-bromate method (described later) in order to determine the butadiene.



Courtesy Industrial and Engineering Chemistry, Analytical Edition

FIG. 48.—Absorption of Ethylene and Propene (Orsat Pipet) into Pure 87 per cent Sulphuric Acid and into same Acid Saturated with Catalysts (Silver and Nickel Sulphates). (Davis and Quiggle.)

The estimation of unsaturated hydrocarbons by the sulphuric acid absorption method has been critically examined by Davis and Quiggle,[62] and some of its limitations have been exposed. The rates of absorption of propylene and of the two straight-chain butylenes (1- and 2-butene) are so close that separation by selective absorption is impossible. On the other hand, separation of ethylene from propylene is obtained by absorption of the latter in 87 per cent sulphuric acid. Saturation of this concentration of acid with silver and nickel sulphates, as recommended by Tropsch and Dittrich[63] was found by Davis and Quiggle to diminish the effectiveness of this acid for separating ethylene from propylene in an Orsat pipette more than one hundredfold. The results on the absorption of ethylene and propylene in an Orsat pipette in pure 87 per cent acid, and in the same acid saturated with silver and nickel sulphates, are shown graphically in Figure 48.

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[60] *Neft. Khoz.*, 1925, **9**, 565; *Chem. Zentr.*, 1926, **1**, 2220; *Brit. Chem. Abs.* **B**, 1926, 394.
[61] Sulphuric acid of 83 to 84 per cent concentration also absorbs 1- and 2-butenes.
[62] *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 39; *cf.* Davis and Schuler, *J.A.C.S.*, 1930, **52**, 721.

A survey of the published work on the estimation of unsaturated hydrocarbons by successive absorptions in graded concentrations of sulphuric acid leads to the conclusion that the process is only applicable to the accurate analytical separation of ethylene from its homologues. With the possible exception of isobutylene, which can be absorbed in about 50 per cent acid, the rates of absorption of gaseous homologues of ethylene are too close to one another for effective separation. Catalysts, such as a mixture of silver or nickel sulphates, added to the sulphuric acid are of value only for the determination of ethylene or total unsaturated hydrocarbons and diminish the effectiveness of separation of the individual members.

It has been recommended that with 87 per cent sulphuric acid the absorptions be timed and repeated and carried out with fresh acid until the rate becomes small and constant, indicating that ethylene is being absorbed. The final result can then be corrected for this ethylene absorption.[64] Manning, King and Sinnatt[65] proposed the following procedure for the analytical separation of ethylene from propylene and higher homologues in gas mixtures obtained by decomposing dibromides with a zinc-copper couple. A portion of the gas is treated successively in the Bone and Wheeler apparatus with 2 cc. of 87 per cent sulphuric acid for 5 minutes at each treatment. The olefins higher than ethylene are absorbed completely in the first 20 minutes (four treatments) at ordinary temperature. After this period the absorption during each 5 minutes treatment becomes small and constant and is due entirely to the ethylene content. A determination of this ethylene absorption rate enables a correction to be made for the ethylene absorbed during the first four treatments (20 minutes).

Dubois[65a] used sulphuric acid in the separation of hydrocarbons in connection with a calorimetric determination. The heats of combustion are determined for the original mixture, the mixture after unsaturated compounds are removed by fuming sulphuric acid, and the mixture from which propylene and higher homologues are removed by 87 per cent sulphuric acid solution.

ANALYSIS OF GASEOUS UNSATURATED HYDROCARBONS BY BROMINATION

A bromine addition method for the estimation of butadiene in gas mixtures, which makes use of the bromide-bromate reagent of Francis,[66] has been described by Dobrjanski.[67] The gas is introduced into an air-tight apparatus containing a solution of potassium bromide and sulphuric acid in water. A weighed quantity of potassium bromate is allowed to react with the liquid with the result that bromine is slowly evolved according to the equation:

$$KBrO_3 + 6KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + KBr + 3Br_2$$

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[63] *Loc. cit.* See also Frey and Yant, *Ind. Eng. Chem.*, 1927, 19, 488; and Carnegie Steel Co., "Methods of Chemists of U. S. Steel Corporation for Sampling and Analysis of Gases," 3rd edition, p. 36.

[64] See, for example, Hague and Wheeler, *Fuel*, 1929, 8, 560; *Brit. Chem. Abs.* B, 1930, 90.

[65] *Dept. Scientific and Industrial Research, Technical Paper* 19, 1928; *Chem. Abs.*, 1928, 22, 1668.

[65a] *Przemysl Chem.*, 1931, 15, 390; *Chem. Abs.*, 1932, 26, 2142.

[66] *Ind. Eng. Chem.*, 1926, 18, 821.

[67] *Petroleum Domain*, 1925, 9, 574; *Chem. Abs.*, 1926, 20, 1577.

The bromine thus produced adds directly to the unsaturated gases, forming dibromides with monolefins and tetrabromides with diolefins. The excess bromine is determined by adding a sufficient quantity of potassium iodide to the solution and titrating the librated iodine with standard thiosulphate solution. From this, the quantity of bromine absorbed by the gas can be calculated. Having determined the total quantity of unsaturated hydrocarbons (by total absorption, e.g., with bromine water), the amount of olefin and diolefins can be calculated from the bromine addition results.

A critical examination of this bromination method for the examination of unsaturated gases and liquid was made by Davis, Crandall, and Higbee.[68] The presence of oxygen was found to interfere with the quantitative titration of acetylenes and probably of some diolefins. A standard procedure was developed by which ethylene and acetylene and some of their higher homologues can be titrated quantitatively by bromide-bromate solution. A measured volume of the gas was introduced into a previously evacuated reaction bottle containing the bromide-bromate solution. Dilute sulphuric acid was added to this from a Mohr burette. By slow addition of the acid, the bromine is liberated gradually and is taken up by the unsaturated compounds as fast as it is formed. In this manner, the concentration of the halogen is kept low throughout the process and substitution reactions are avoided. The excess bromine can be estimated in the usual way, with potassium iodide and thiosulphate solution. Under these conditions, monolefins absorb two equivalents of bromine, whereas acetylenes and diolefins absorb four equivalents.

A considerable number of workers have used the bromine addition products of unsaturated hydrocarbons for the qualitative or rough quantitative detection of individual unsaturated hydrocarbons.[69] Manning, King and Sinnatt[70] developed a method of evaluation of unsaturated gases which depends upon bromination to a mixture of dibromides, followed by refractionation of these dibromides and regeneration of the unsaturated products. A large volume of gas is usually necessary for the determination, and sufficient should be used to furnish at least 100 grams of bromine addition products. The gas is first scrubbed with gas oil to remove vapors of higher normally liquid hydrocarbons and then passed through two absorption bottles, each containing 25 to 75 cc. of bromine covered with 100 cc. of 10 per cent potassium bromide solution. The bottles should be cooled with ice and it is desirable to condense any bromides, carried forward with the gas stream, in two spiral condensers cooled in a freezing mixture of ice and salt. The bromine compounds are subsequently mixed, washed with dilute caustic soda and water, respectively, dried, and fractionally distilled under 20 mm. pressure. The following fractions are collected:

(1) Up to 80° C. at 20 mm., containing all the ethylene and propylene dibromides, and most of the butylene dibromides.
(2) 80° to 130° C. at 20 mm., which contains remaining butylene dibromides together with bromine derivatives of higher olefins.
(3) Residue, which consists, in the case of cracking gas, almost entirely of butadiene tetrabromide.

The procedure recommended involves the liberation of the mixed olefins from known weights of fractions (1) and (2) by means of a zinc-copper couple, followed by an examination of the gases produced, as follows:

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[68] *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 108.

[69] Armstrong and Miller, *J.C.S.*, 1886, **49**, 74. Sinnatt and Slater, *Analyst*, 1920, **45**, 85; *Chem. Abs.*, 1920, **14**, 2407. Arnold, *Z. angew. Chem.*, 1924, **37**, 85; *Chem. Abs.*, 1924, **18**, 1894. Hock, *Z. angew. Chem.*, 1924, **37**, 252; *J.S.C.I.*, 1924, **43**, 5468. Schütz, Buschmann and Wissebach, *Ber.*, 1923, **56B**, 1091.

[70] *Dept. Scientific and Industrial Research, Technical Paper* **19**, 1928; *Chem. Abs.*, 1928, **22**, 1668.

(1) The total olefin content is determined by absorption in fuming sulphuric acid or bromine water.

(2) A second portion of the gas is burned completely over copper oxide at 700° C. and the carbon dioxide produced is determined.

(3) Another portion of the gas is treated successively with 2 cc. of 87 per cent sulphuric acid (5 minutes for each treatment). The olefins higher than ethylene are absorbed completely in 20 minutes at ordinary temperatures. After this period the absorption during 5 minutes becomes small and constant and is due to ethylene only, as before stated.

From the above data it is possible to calculate the actual percentage of the individual olefins in a mixture of ethylene, propylene and butylenes.

The butadiene content of the original gas may also be estimated by extracting the residue (3) with hot alcohol and cooling the filtered solution to 0° C., when the higher melting crystalline butadiene tetrabromide separates out quantitatively and can be filtered rapidly and weighed. Under these conditions of bromination, a second (lower-melting) butadiene tetrabromide is also produced in about equal amount so that to obtain the total butadiene tetrabromide present in the residue, the weight of the higher-melting form must be doubled. (See Chapter 27.)

Roginski and Rathmann[70a] analyzed a mixture of cyclopropane and propylene by taking advantage of the rapidity with which the latter is absorbed by aqueous iodine-bromine solution. Under the same conditions cyclopropane is absorbed but slowly.

SPECIAL METHODS OF ANALYSIS OF VARIOUS UNSATURATED GASES

For the analytical absorption of acetylene, Hague and Wheeler[71] employed an ammoniacal solution of silver chloride and conducted the absorption for 2 minutes in the Bone and Wheeler[72] apparatus. This reagent also tends to absorb quantities of olefins and diolefins, however.

As previously indicated, ethylene is best absorbed either in bromine water or by concentrated sulpuhuric acid or fuming acid. Morris,[73] however, recommended a 20 to 40 per cent aqueous solution of silver nitrate for absorbing ethylene from gas mixtures. The ethylene may be recovered from the concentrated silver salt solution by evacuation. Heymans[74] determined ethylene in cracked products (after absorption of carbon dioxide by potassium hydroxide and higher olefins by 87 per cent sulphuric acid) by absorbing it in a solution of mercuric nitrate saturated with sodium nitrate, after which benzene vapors are estimated by treatment with bromine water.

According to Nametkin,[75] unsaturated gaseous hydrocarbons are quantitatively absorbed from gas mixtures in a concentrated aqueous solution of potassium permanganate without the saturated hydrocarbons being affected. This method is satisfactory for the determination of the total unsaturated hydrocarbon content of gas mixtures but special apparatus must be used since the permanganate solution attacks mercury.

For the estimation and analytical separation of the isomeric butenes no simple methods are available. All three unsaturated hydrocarbons are found in frac-

[70a] *J.A.C.S.*, 1933, 55, 2800.

[71] *J.C.S.*, 1929, 383.

[72] *Loc. cit.*

[73] *J.A.C.S.*, 1929, 51, 1460.

[74] *J. Inst. Pet. Tech.*, 1930, 16, 663; *Chem. Abs.*, 1931, 25, 1066.

[75] *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1423; *Bull. soc. chim.*, 1914, 16, 126; *J.S.C.I.*, 1914, 33, 1229; *Chem. Abs.*, 1914, 8, 324.

tions of cracking gas boiling at about 0° C. Of these, isobutene is by far the more reactive. Dobrjanski[76] showed that it can be separated from the other two by absorption in 63 per cent sulphuric acid. This separation is complicated, however, by the presence of certain other hydrocarbons boiling in the same range, especially butadiene. In the presence of butadiene, isobutylene is best estimated by absorption in sulphuric acid of concentration lower than 60 per cent (satisfactorily in 45 to 46 per cent).

Frey and Yant[77] determined isobutylene in mixtures of the three butenes (obtained by fractionation of low-temperature carbonization gas) by absorption in a mixture of 2 volumes of sulphuric acid (specific gravity 1.84) and 1 volume of water.

Investigations of mixtures of butenes as their dibromides have been made by a number of workers. Frey and Yant[77] carried out the bromination of a butene mixture by adding bromine, drop by drop with agitation, into the liquid hydrocarbon mixture previously cooled to —80° to —100° C. until addition was nearly complete. The temperature was then allowed to rise to —20° C. and the addition of bromine continued until the color persisted. The dibromides were then distilled under reduced pressure at temperatures below 60° C. (residue temperature). For the determination of 1-butene in this mixture, Frey and Yant employed a method in which the dibromide mixture was heated with a 15 per cent solution of potassium hydroxide in absolute alcohol at about 100° C. in a sealed tube. Under these conditions, only the dibromide of 1-butene is decomposed, whereas the dibromides of 2-butene and isobutene are unattacked.[78] 1-Butene dibromide is decomposed to the extent of about 51 per cent (this yield is roughly constant for periods of heating varying from 2 to 5 hours) into ethylacetylene according to the reaction:

$$CH_2BrCHBrCH_2CH_3 \longrightarrow CH{\equiv}CCH_2CH_3 + 2HBr$$

After cooling the reaction mixture to —75° C., the contents were slowly distilled through a condenser into an excess of 5 per cent alcoholic silver nitrate. Two volumes of water were added to decrease the solubility of the precipitated $C_4H_5Ag_2NO_3$, which was filtered off, washed with water and dissolved in dilute nitric acid. The silver was then determined by titration with standard potassium thiocyanate solution, with ferric nitrate as indicator.

A qualitative method of examining butene mixtures, which consists in a careful fractionation of the dibromides under 50 mm. pressure, has been described by Lucas, Dillon and Young.[79] Bromination of the butene mixture was effected by slowly introducing bromine into the well-agitated liquid butene mixture, cooled to —15° to —20° C.

According to Dillon, Young and Lucas,[79a] mixtures of the three normal butenes can be analyzed by means of the densities of their dibromides and the reaction rate of these latter compounds with potassium iodide. The method depends on the fact that each of the three butenes is quantitatively converted to the dibromide by treatment with bromine, and each of the dibromides has a different second-order reaction rate with potassium iodide in methanol at 75° C. A combination of the reaction rate with the density is sufficient for the analysis of any mixture of the three dibromides, and from this the content of the three butenes can be computed.

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[76] *Loc. cit.*

[77] *Ind. Eng. Chem.*, 1927, 19, 488.

[78] Wislicenus and Schmidt, *Ann.*, 1900, 313, 212; *Chem. Soc. Abs.*, 1901, 80 (1), 1.

[79] *J.A.C.S.*, 1930, 52, 1949.

[79a] *J.A.C.S.*, 1930, 53, 1953.

Davis[80] indicated the possibility of developing a method of analysis of mixtures of 1- and 2-butene by taking advantage of different rates of bromination of these olefins in carbon tetrachloride thoroughly dried over phosphorus pentoxide. In a perfectly dry medium, in the absence of strong light, 1-butene and 2-butene react at different rates, the former slowly and at approximately the same rate as propylene and the latter more rapidly and at about the same rate as isobutene.

Several methods of estimating butadiene in gas mixtures have already been discussed in Chapter 27. Tropsch and Mattox[81] developed a method for the determination of butadiene in complex gas mixtures, from which the diolefin is absorbed in molten maleic anhydride at 100° C.

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[80] *J.A.C.S.*, 1928, 50, 2769.

[81] *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 104.

Chapter 50

Methods of Analysis of Gasoline and Other Petroleum Distillates

Petroleum oils consist essentially of complex mixtures of hydrocarbons but also contain as minor constituents oxygenated bodies, nitrogen and sulphur compounds and, to a very small extent, mineral matter (see Chapter 1). All non-hydrocarbon materials may consequently be classed as impurities, since all or part of them must be removed in refining because of their injurious character in various industrial applications of petroleum fractions. Thus, gasoline for use in internal combustion engines is usually made substantially free of sulphur compounds, because of the offensive odor of some of these substances and the corrosive nature of some of the products of combustion.[1] Kerosene for use in wick-fed lamps for domestic purposes is generally refined to remove all material which is likely to give objectionable odors. It is therefore convenient to consider, first of all, the analysis and examination of refined petroleum oils, i.e., those containing but small amounts of the impurities mentioned above.

HYDROCARBON ANALYSIS

Petroleum oils generally consist of mixtures of the four principal classes of hydrocarbons—namely, olefin, aromatic, naphthene and paraffin hydrocarbons. The relative amounts of these types of hydrocarbons in any oil vary with its source and, to a lesser extent, with the methods used in refining. For example, as has been pointed out in Chapter 1, the distillates from Appalachian petroleums consist almost entirely of paraffins, many Russian petroleums yield distillates containing a preponderance of naphthenes, and certain other petroleums give volatile fractions containing appreciable proportions of aromatic hydrocarbons. Of these classes, the paraffins and naphthenes, with few exceptions, are the predominating ones.

Olefin hydrocarbons are not found in crude petroleums, but only in their distillates. Light oils obtained by cracking heavier oils contain unsaturated aliphatic hydrocarbons, the amount depending upon the type of oil being cracked and the temperature and pressure employed in the process. Thus gasolines obtained by cracking heavy oils in the liquid phase may contain up to 20 per cent of olefin hydrocarbons, whereas those resulting from cracking in the vapor phase, i.e., at a higher temperature, may contain as much as 60 per cent of these hydrocarbons. Cracked distillates also contain appreciable proportions of aromatic hydrocarbons.

It is desirable from many points of view to be able to determine the proportions of the various hydrocarbons in any petroleum oil or distillate. With higher fractions this assumes importance, because of the well-known antiknock effect

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[1] See Chapter 19.

Acknowledgment is made of assistance rendered by Dr. D. A. Howes in connection with the preparation of parts of this chapter.

of aromatics and olefins in gasoline (Chapter 44), the potential gum- and resin-forming properties of some of the more unstable olefins (Chapter 40), and the characteristic of aromatics of imparting a smoky flame to kerosenes.[2] Developments in the utilization of petroleum fractions as raw materials in chemical synthesis necessitate still more careful study in this direction.

The problem of devising methods for the determination of aromatic, olefin, naphthene and paraffin hydrocarbons in petroleum distillates is complicated by the fact that the chemical reactivity of the hydrocarbons of any class generally changes comparatively rapidly with rise in molecular weight and boiling point. Reactions which proceed rapidly with the lower members of the series will often proceed only with difficulty with higher homologues. Thus, the basis of a well-known method for the determination of olefins is the reaction of these hydrocarbons with halogens—bromine or iodine—and although the halogenation occurs readily with the lower olefins, e.g., the pentenes and hexenes, it is appreciably slower with, for example, the diamylenes and triamylenes. Under conditions which convert these latter hydrocarbons quantitatively into halogen derivatives, there is a possibility of the halogen attacking hydrocarbons of other classes. Another factor adding to the difficulties of such analyses is the fact that as the boiling points of the hydrocarbons increase, the members of the four hydrocarbon classes gradually approach one another in chemical properties. Thus there is a great similarity between the higher α-olefins and the paraffins. Because of this, the methods of analysis are only applicable to petroleum distillates boiling up to 300° C., unless otherwise stated. With distillates boiling above 300° C., the chemical properties of the individual classes are so nearly identical that it is difficult to differentiate sharply between them.

ESTIMATION OF UNSATURATED HYDROCARBONS BY ABSORPTION IN SULPHURIC ACID

It is usual to class the aliphatic and naphthenic olefins, as well as those aromatics which contain an unsaturated aliphatic side-chain, as unsaturates. The determination of such hydrocarbons may be accomplished by methods which depend upon the following:

(1) Solution in sulphuric acid.
(2) Absorption of halogens.
(3) Reaction with mercury salts.
(4) Other typical reactions of unsaturated hydrocarbons.

Unsaturated hydrocarbons are attacked by sulphuric acid of lower concentration than that necessary for aromatic and other hydrocarbons. This fact has long been used as a basis for a rapid and convenient, if not accurate, analytical method. The reaction of sulphuric acid with unsaturated hydrocarbons is a complex process, details of which have been previously discussed in Chapters 12, 14, 16, 26, 46 and 49. It is sufficient here to repeat that this reaction may yield (depending upon the conditions employed, e.g., time of contact, temperature, and concentration of acid) polymers of the original hydrocarbons, alkylsulphuric esters, alcohols, and oxidation products. The polymers are completely miscible with the oil layer unless an acid of such strength is used that they are removed, whereas the alkylsulphuric esters are only partly soluble in the acid layer. These are the sources of the major errors to which the acid method is subject.

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[2] The influence of the chemical composition of kerosene and its burning properties was discussed by Virobyantz and Sentzov, *Neft. Khoz.*, 1932, **22**, 331; **23**, 91; *Chem. Abs.*, 1933, **27**, 1741; Grote and Hundsdörfer, *Petroleum Z.*, 1932, **28** (28), 9; *Brit. Chem. Abs.* **B**, 1932, 1016; Danaila, *Petroleum Z.*, 1933, **29** (7), 1; *Brit. Chem. Abs.* **B**, 1933, 338.

The choice of the strength of acid to employ must of necessity be a compromise. As pointed out in Chapter 26, the polymers of the unsaturated hydrocarbons still contain a double bond but are much more resistant to sulphuric acid than the parent olefins and consequently a more concentrated acid is required to remove them. On the other hand, the strength of the acid must not be high enough to attack aromatic hydrocarbons. Opinion on this point is divided. Ormandy and Craven[3] found, by treating gasolines with sulphuric acid of various strengths, that the density and refractive index of the residue rose until the acid strength reached 88 per cent. This they ascribed to removal of unsaturates and formation of polymers. With higher strengths of acid, extraction of aromatics occurred and the density and refractive index fell. Hence, they concluded that 88 per cent appears to be the critical strength of acid at which extraction of unsaturates approaches completion and the extraction of aromatics begins.[4] This work has been confirmed by Moore and Hobson,[5] who found that 88 to 90 per cent acid was essential for the complete removal of unsaturates. The strength of acid used for this estimation should be adjusted, however, to the kind of light oil under examination. In general, gasolines obtained by distillation from crude oils, i.e., straight-run gasolines—which generally contain only traces of unsaturated hydrocarbons—need treatment with a stronger acid than gasolines produced by cracking. For example, in the method proposed by Riesenfeld and Bandte,[6] 100 per cent sulphuric acid is used for determining the unsaturates in medium and heavy straight-run gasolines, 94 per cent acid for the lighter gasolines of this type,[7] and 85 per cent sulphuric acid for cracked gasoline.

Because of the polymerization which always takes place to some extent when unsaturated hydrocarbons are treated with sulphuric acid, it is not sufficient to measure only the loss in volume of the sample when shaken with acid. A result obtained in that manner is low by the amount of polymers remaining dissolved in the oil layer. A correction to be applied for this error was introduced by Egloff and Morrell,[8] who recommended the redistillation of the acid-treated sample, after washing with water and caustic soda, to estimate the amount of polymers formed. If $a =$ per cent volume loss on treating with acid, and $b =$ amount of polymerized material obtained on redistillation, the content of unsaturated hydrocarbons is $a + b$. Unfortunately, however, although this method gives more accurate results than the simpler method in which loss in volume on acid treatment alone is measured, it does not account for the polymerized material formed which boils within the original boiling range of the oil treated. For instance, trimethylethylene, boiling at 38° C., polymerizes to a mixture of diamylenes boiling between 150° and 160° C., whereas gasolines have a final boiling point of 190° to 200° C. Consequently, if a gasoline of this boiling range containing trimethylethylene is analyzed according to the method of Egloff and Morrell, the polymerization of this hydrocarbon is not measured, and the result is low by this amount. The dipolymers of the hexenes boil between 190° and 200° C., whereas the dipolymer of isoheptene has a boiling point of 220° to

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[3] *J. Inst. Pet. Tech.*, 1926, 12, 68; *Chem. Abs.*, 1926, 20, 2581; see also *J. Inst. Pet. Tech.*, 1927, 13, 844; *Brit. Chem. Abs.* B, 1928, 148; *J.S.C.I.*, 1928, 47, 317T; *Chem. Abs.*, 1929, 23, 2148; *J. Inst. Pet. Tech.*, 1931, 17, 185; *Chem. Abs.*, 1931, 25, 2841.

[4] *Cf.* Brame, *J. Inst. Pet. Tech.*, 1926, 12, 48; *Brit. Chem. Abs.* B, 1926, 395; *J. Inst. Pet. Tech.*, 1926, 12, 221; *Chem. Abs.*, 1927, 21, 1703.

[5] *J. Inst. Pet. Tech.*, 1925, 11, 587; *Chem. Abs.*, 1926, 20, 1712.

[6] Erdöl und Teer., 1926, 2, 491; *Chem. Abs.*, 1926, 20, 3346; see also Erdély and Almási, *Brennstoff-Chem.*, 1927, 8, 358; *Chem. Abs.*, 1928, 22, 3039.

[7] Winkler (*Przemysl Chem.*, 1930, 14, 1; *Brit. Chem. Abs.* B, 1930, 272) recommended 92 to 94 per cent acid for the absorption of unsaturated constituents from straight-run benzine. However, 4 per cent of unsaturates are unabsorbed when this concentration of acid is used for a benzine produced by cracking. Nametkin and Robinzon (*Neft. Khoz.*, 1929, 14, 775; *Chem. Abs.*, 1929, 23, 3802) also observed that aromatic hydrocarbons were removed by 98 per cent sulphuric acid at 0° C.

[8] *Ind. Eng. Chem.*, 1926, 18, 354. *Cf.* Egloff, *Chem. Met. Eng.*, 1917, 16, 262.

224° C. and a mixture of 1- and 2-octenes gives a mixture of dipolymers boiling between 275° and 285° C. A more accurate method consists in fractionating the gasoline into narrow cuts, treating each separately with acid and measuring the natural loss and then redistilling each fraction separately to estimate the extent of polymerization. This procedure is tedious and time-consuming, however.

For the estimation of unsaturated hydrocarbons in kerosenes, Carpenter[9] recommended the use of 4 volumes of 83 per cent sulphuric acid followed by redistillation to estimate the amount of polymers formed.

The formation of olefin polymers is not, however, the only difficulty in this general method of estimation. It was observed by Krämer and Spilker[10] that, in the presence of sulphuric acid, styrene and the xylenes condense to form styroxylenes. Later, Brochet[11] found that aliphatic unsaturated hydrocarbons condensed with benzene homologues in the same way, e.g., benzene and hexene give hexylbenzene. Toluene and xylene also condense similarly and other unsaturates probably react like hexene. It is possible for condensations of this type to take place in the methods of analysis described above.

Other reactions also may occur at the same time. Unsaturated hydrocarbons containing more than one double bond are more easily polymerized than monolefins. Thus, allylene in contact with concentrated sulphuric acid yields trimethylbenzene and crotonylene gives hexamethylbenzene.[12] Methylcyclohexene produces methylcyclohexane and two isomeric diheptenes, together with some toluene.[13]

These considerations show that the estimation of unsaturated hydrocarbons by absorption in sulphuric acid gives but an approximately correct estimation even under the most favorable conditions, because the chemical reactions involved are so numerous and complex and because hydrocarbons of other groups can react under the conditions employed.

ESTIMATION OF UNSATURATED HYDROCARBONS BY HALOGENATION

The ease with which unsaturated hydrocarbons absorb halogens has led to the development of many methods of estimation based upon this behavior. The reaction involved is a simple addition, except in aqueous solution, when part of the halogen reacts with water to give a hypo-acid which adds to the olefin, producing a halogen derivative of an alcohol. Thus, with hypobromous acid:

$$RCH{=}CH_2 + HBrO \longrightarrow RCHBrCH_2OH \text{ (see Chapter 20).}$$

When addition of two halogen atoms takes place a simple titration indicates the "double-bond equivalent" of the unsaturates present. From this may be obtained an approximate value for the unsaturation or unsaturated hydrocarbon content of the sample under examination. It is not possible to estimate accurately the unsaturated hydrocarbon content in this way unless the molecular weight or average molecular weight of the constituents is known. Results are usually expressed in terms of bromine or iodine numbers which are defined as the number of centigrams of the halogen absorbed per gram of material.

Substitution of halogen atoms often proceeds at the same time as the halogen addition, as is shown by the evolution of hydrogen bromide. It is probable that the ease with which substitution occurs increases with rising molecular weight of the hydrocarbons. The presence of moisture and the influence of light-rays affect the course of the reaction and the time required for its completion. Thus, Davis[14] found that the bromination of ethylene takes hours, and even days, to reach completion if moisture and light are excluded. He also observed that temperature has little effect on the dry bromination of trimethylethylene or diisobutene, and that large amounts of hydrogen bromide are evolved.

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[9] *J. Inst. Pet. Tech.*, 1928, 14, 446; *Brit. Chem. Abs.* B, 1928, 736.

[10] *Ber.*, 1890, 23, 3169; *Chem. Soc. Abs.*, 1891, 60, 206.

[11] *Compt. rend.*, 1893, 117, 115; *Chem. Soc. Abs.*, 1893, 64, 635.

[12] Schrohe, *Ber.*, 1875, 8, 18, 367; *Chem. Soc. Abs.*, 1875, 28, 625; Michael, *J. pr. Chem.*, 1899, (2) 60, 441; Almedingen, *J. Russ. Phys.-Chem. Soc.*, 1881, 13, 392; see Chapter 28.

[13] Maquenne, *Ann. chim.*, 1893, (6) 28, 279; *Bull. soc. chim.*, 1893, (3) 9, 129; *Chem. Soc. Abs.*, 1893, 64, (1), 635; *cf.* Kishner, *J. Russ. Phys.-Chem. Soc.*, 1908, 40, 676, 687.

The more common methods of estimating unsaturated hydrocarbons by halogen absorption are those developed by Hübl,[15] Wijs[16] and Hanus,[17] but these methods, though of considerable use in the examination of animal, fatty and vegetable oils, are not entirely satisfactory for the examination of petroleum oils. The method of Hübl makes use of a solution of iodine and mercuric chloride in alcohol and that of Wijs, a decinormal solution of iodine monochloride in glacial acetic acid. The Hanus reagent consists of a solution of bromine and iodine in molecular proportions in glacial acetic acid. Of these methods, that of Hanus is still used to some extent. However, it is being replaced rapidly by newer methods.

Another halogenation method, that proposed by McIlhiney,[18] which permits the separate determination of halogen addition and substitution, is dependent upon the fact that for each atom of hydrogen replaced by bromine, one molecule of hydrogen bromide is formed. By estimation of this free acid, therefore, as well as the total amount of bromine absorbed, data are obtained for calculating both the bromine taken up by direct addition and that taken up by substitution. The estimation of the hydrobromic acid is accomplished by the addition of potassium iodate to the solution after the excess bromine has been destroyed by potassium iodide and sodium thiosulphate. The reaction ($KIO_3 + 5KI + 6HBr \rightarrow 6KBr + 3H_2O + 3I_2$) is brought about by the addition of a small amount of dilute sulphuric acid.

Experiences with the McIlhiney method of determining unsaturation have been described by Morrell and Egloff,[19] Dean and Hill,[20] Waterman, Spijker and van Westen[21] and Waterman and van Westen.[22]

The reagent used in a method developed by Francis[23] is a standard solution of potassium bromide and bromate, which in acid solution produces bromine:

$$KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + 3Br_2,$$

the rate depending upon the strength of acid employed. By making the solution only slightly acid, bromine can be generated slowly. With vigorous shaking the bromine can be consumed fast enough to keep it at a low concentration in the solution and thus prevent substitution reactions. It is important, for accurate results, that the concentration of free bromine be maintained low. Precise methods for the determination are as follows:

A slight excess (usually not more than 1 cc. as estimated by a trial titration) of the bromide-bromate solution, containing 14 grams of potassium bromate and 80 grams of potassium bromide per liter, is measured into a small Erlenmeyer flask and a pipetted sample of the oil to be examined is added. The solution is quickly acidified with about 5 cc. of 10 per cent sulphuric acid and the flask is stoppered and shaken for one minute as vigorously as may be necessary to keep the color of the solution a pale yellow. If the color is dark yellow in spite of vigorous shaking, too much bromide-bromate solution has been added, and the analysis should be considered only a trial titration. In any case, to complete the liberation of bromine, 15 cc. more of acid are added and the shaking is continued for another minute. If the solution remains completely colorless, a little more bromide-bromate solution is added. The final color should be light yellow. One or 2 cc. of saturated potassium iodide solution are then added, and the liberated iodine is titrated with thiosulphate in the usual way. Results may be calculated with the equation:

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[14] *J.A.C.S.*, 1928, **50**, 2769; see also Chapter 49.

[15] *Dinglers Polytech. J.*, 1884, **253**, 281; *J.S.C.I.*, 1884, **3**, 641.

[16] *Ber.*, 1898, **31**, 750; *J.S.C.I.*, 1898, **17**, 699.

[17] *Z. Nahr.-Genussm.*, 1901, **4**, 913; *J.S.C.I.*, 1901, **20**, 1246. Ormandy and Craven (*J. Inst. Pet. Tech.*, 1925, **11**, 533) used the Hanus method for determining the unsaturated constituents of various light oils but obtained results which were higher than those from absorptions in sulphuric acid.

[18] *J.A.C.S.*, 1899, **21**, 1084.

[19] *Ind. Eng. Chem.*, 1925, **17**, 1259.

[20] *U. S. Bur. Mines, Tech. Paper* 181, 1917; *Chem. Abs.*, 1918, **12**, 1120.

[21] *Rec. trav. chim.*, 1929, **48**, 612; *Brit. Chem. Abs.* **A**, 1929, 907.

[22] *Rec. trav. chim.*, 1929, **48**, 637; *Brit. Chem. Abs.* **A**, 1929, 921.

[23] *Ind. Eng. Chem.*, 1926, **18**, 821.

$$N=\frac{0.08}{VD}(T_1N_1-T_2N_2),$$

in which N = Bromine number in grams per gram of sample
V = Volume of the sample used in cc.
D = Density of sample in grams per cc.
T_1 = Volumes in cc. of the bromide-bromate solution used in titration
N_1 = Normality of the bromide-bromate solution
T_2 = Volume in cc. of the thiosulphate solution used in titration
N_2 = Normality of the thiosulphate solution.

The content of unsaturated hydrocarbons can be calculated from the bromine number with the equation:

$$\%\ \text{Unsaturates}=\frac{MN}{160}$$

in which M = Mean molecular weight of the unsaturated hydrocarbons
N = Bromine number calculated as above.

If the unsaturated hydrocarbons are evenly distributed throughout the boiling range of the light oil examined, which is rarely the case, the mean molecular weight is approximately equal to 54 plus half the mean boiling point in degrees Centigrade.

Francis[24] checked this method of analysis by examining pure hydrocarbons and mixtures of straight-run and cracked gasolines. The results obtained were quite satisfactory. The method has also been examined critically by Cortese,[25] who concluded that it can be used for aliphatic olefins and diolefins, whether conjugated or otherwise, but that the method does not give accurate results with certain compounds with ring structures or with substances of unknown constitution. A modification of the Francis method of bromine number determination was used by Bacon[26] for the estimation of the unsaturation of lubricating oils. The original method gave difficulty with dark colored oils because it was impossible to determine when all the bromine was absorbed and when the last traces of iodine had reacted completely with the thiosulphate. The modification adopted by Bacon consists of adding to the sample of lubricating oil to be tested 10 cc. of pure benzene or gasoline of known unsaturated content. A slight excess of bromide-bromate solution is then added, as shown by the color of the water layer, with potassium iodide as indicator. The visible end point is then passed in titration with thiosulphate, the two layers are allowed to separate and starch is added to the lower water layer so that a titration with iodine indicates the excess thiosulphate. Vigorous shaking is essential throughout the determination.

A 4 per cent by volume solution of bromine in carbon tetrachloride has been used in diffused light by Morrell and Levine[27] for the determination of olefins. The solution is standardized against a sample of which the olefin content is known and the titration is conducted under identical conditions. For the estimation of unsaturated compounds, Rosenmund and Kuhnhenn[28] suggested the use of pyridine sulphate dibromide, and Galle[29] recommended an alcoholic iodine or an aqueous chloramine (sodium-p-toluenesulphochloroamide) solution. A method, devised by Angeli, Alessandri and Pegna,[30] depends upon the color change produced by the oil in the presence of nitrosobenzene.

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[24] *Loc. cit.*
[25] *Rec. trav. chim.*, 1929, **48**, 564; *Brit. Chem. Abs.* **A**, 1929, 789.
[26] *Ind. Eng. Chem.*, 1928, **20**, 970.

The bromine absorption method of estimating unsaturation is of special use in determining the purity of unsaturated hydrocarbons of which the molecular weight is known. Wilkinson[31] employed the McIlhiney method of bromine number determination as a check on the purity of a series of α-olefins with complete success.

The possible action of bromine upon members of the other hydrocarbon classes must not be neglected. Bacon[32] asserted that benzene is brominated somewhat when exposed to strong light or sunlight, even under the action of only small concentrations of bromine. He found that pure benzene had a bromine number of 0.027 in moderate light and 18.00 in sunlight, as determined by the Francis method. Gustavson[33] observed that benzene was attacked by dry bromine, whereas the action with bromine containing moisture and hydrobromic acid was even more pronounced. Higher homologues of benzene react still more readily with bromine. Bigot and Fittig[34] stated that, even with efficient cooling, bromine acts upon amylbenzene and more rapidly upon amyltoluene and amylxylene. Bromine also reacts with a few naphthenes. According to Gustavson,[35] dry bromine reacts slowly upon cyclopropane, the reaction also being accelerated by the presence of water and hydrobromic acid. The substituted cyclopropanes are attacked more readily,[36] but cyclobutane is stable towards bromine in chloroform solution,[37] in which respect it resembles the cyclopentanes and cyclohexanes.

ESTIMATION OF UNSATURATED HYDROCARBONS BY REACTION WITH MERCURIC SALTS

A well-known reaction of the unsaturated hydrocarbons is that with mercuric salts.[38] Depending upon the molecular weight and configuration of the hydrocarbons, reaction can take place in two different ways: the hydrocarbons are either oxidized and destroyed or else they form complex addition compounds. Paraffin and naphthene hydrocarbons do not react in this way. Although some aromatic hydrocarbons also react to a slight extent, the reaction has been used as a basis for an analytical estimation of unsaturated hydrocarbons.

The gaseous olefins readily form complex addition compounds with mercuric salts at ordinary temperatures, from which they may be recovered by the action

[27] *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 319.

[28] *Z. Nahr. Genussm.*, 1923, **46**, 154; *Chem. Abs.*, 1924, **18**, 477; see also Poggi, *Gior. chim. ind. applicata*, 1928, **10**, 601; *Chem. Abs.*, 1929, **23**, 3565.

[29] *Z. angew Chem.*, 1931, 474.

[30] *Atti. accad. Lincei*, 1910, **19** (1), 650; *Chem. Abs.*, 1910, **4**, 2457. *Cf.* Poggi, *loc. cit.*

[31] *J.C.S.*, 1931, 3057.

[32] *Loc. cit.*

[33] *Compt. rend.*, 1900, **131**, 273; *Chem. Soc. Abs.*, 1900, **78** (1), 535; *J. pr. Chem.*, 1900, **62**, 273; *Chem. Soc. Abs.*, 1901, **80** (1), 3.

[34] *Ann.*, 1867, **141**, 160.

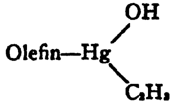
[35] *Loc. cit.*

[36] Aschan, "Chemie der alicyklischen Verbindungen," Vieweg und Sohn, Braunschweig, 1905, 428.

[37] Willstätter and Bruce, *Ber.*, 1907, **40**, 3989; *Chem. Abs.*, 1908, **2**, 259.

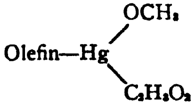
[38] Balbiano and Paolini, *Chem. Ztg.*, 1901, **25**, 932; *Chem. Soc. Abs.*, 1902, **82** (2), 109; *Ber.*, 1902, **35**, 2994; *J.S.C.I.*, 1902, **21**, 1293.

of acid.[39] Unsaturated hydrocarbons of low molecular weight react easily at ordinary temperatures, but those of higher molecular weight, e.g., octene and diamylene, react only slowly on boiling. According to Hugel and Hibou,[40] when aqueous solutions of mercuric acetate are used, the addition compounds have the general formula



$$\text{Olefin—Hg}\begin{matrix}\diagup\ \text{OH}\\ \diagdown\ C_2H_3O_2\end{matrix}$$

The higher-boiling olefins can be made to react more rapidly when methanol is used as a solvent. In this case the addition compounds have the formula



$$\text{Olefin—Hg}\begin{matrix}\diagup\ \text{OCH}_3\\ \diagdown\ C_2H_3O_2\end{matrix}$$

Hugel and Hibou prepared the addition compounds of olefins as high as hexadecene. Mercuric acetate was used in their experiments, although mercuric sulphate, palmitate, and stearate also react. The mercuric salts that are not hydrolyzed, e.g., mercuric cyanide, do not react in this manner. The reaction with mercuric salts unfortunately is not applicable to all olefins. Ethylene derivatives in which four radicals are attached to the unsaturated carbon atoms (e.g., tetramethylethylene) do not react. Hugel and Hibou also found that the addition compounds formed have a variable composition, depending upon the relative proportions of hydrocarbon and mercuric salt taken.

A method for the quantitative estimation of unsaturated hydrocarbons based on their behavior with mercuric salts has been proposed by Tausz.[41] The sample of oil to be analyzed is first shaken with a saturated solution of mercuric acetate and then refluxed with the same reagent to attack the more resistant hydrocarbons. When the reaction is complete the oil is washed with sodium hydroxide and sodium bisulphite solutions and the loss in volume is taken as the unsaturated hydrocarbon content. A correction is applied for evaporation loss.

Brame and Hunter[42] attempted to use the reaction with mercuric salts for the identification and separation of olefins in cracked gasolines. They abandoned the method in favor of one involving bromination because they were unable to obtain quantitative yields of the addition compounds. It was also observed that when the mercury compounds were decomposed with acid, large quantities of hydrocarbons were destroyed and lost. Manning and Shepherd[43] found that a saturated aqueous solution of mercuric acetate only absorbed about 70 per cent of the unsaturated hydrocarbons in light oils obtained from the low-temperature carbonization of coal. With the lowest-boiling fractions, however, absorption of unsaturated hydrocarbons was almost complete. The solution of mercuric acetate absorbed and retained about 1 per cent of aromatic hydrocarbons.

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[39] Hofmann and Sand, *Ber.*, 1900, **33**, 1340; *Chem. Soc. Abs.*, 1900, **78** (1), 384; *Ber.*, 1900, **33**, 1353; *Chem. Soc. Abs.*, 1900, **78** (1), 385; *Ber.*, 1900, **33**, 2692; *J.S.C.I.*, 1900, **19**, 1034; Sand, *Ann.*, 1903, **329**, 135; *Chem. Soc. Abs.*, 1904, **86** (1), 22; Deniges, *Compt. rend.*, 1898, **126**, 1145; *Chem. Soc. Abs.*, 1898, **74** (1), 546; *Compt. rend.*, 1898, **126**, 1868; *J.S.C.I.*, 1898, 17, 790.

[40] *Chimie et industrie*, Spec. No. 296, Feb. 1929; *Chem. Abs.*, 1929, **23**, 3898.

[41] Tausz and Pfeiffer, *Proc. Int. Petroleum Commission, Vienna*, 1912; *Chem. Abs.*, 1914, **8**, 569; Tausz, *Petroleum Z.*, 1918, **13**, 649; *J.S.C.I.*, 1919, **38**, 4A; *Chem. Abs.*, 1919, **13**, 1146; Tausz and Wolf, *Z. angew. Chem.*, 1919, **32**, 317; *Chem. Abs.*, 1920, **14**, 621.

[42] *J. Inst. Pet. Tech.*, 1927, **13**, 794; *Brit. Chem. Abs.* **B**, 1928, 178.

[43] *Dept. Sci. Ind. Res., Fuel Research, Technical Paper* **28**, 1930; *Brit. Chem. Abs.* **B**, 1931, 284; *Chem. Abs.*, 1931, **25**, 396.

OTHER METHODS FOR THE ESTIMATION OF UNSATURATED HYDROCARBONS

Numerous other methods have been suggested for the determination of unsaturated hydrocarbons in mixtures containing other hydrocarbons. Faragher, Morrell and Levine[44] proposed a two-stage procedure in which the combined olefin and aromatic content is first determined. The aromatic content is then estimated by nitration. The difference between these two values is taken as the olefin content.

The combined olefin and aromatic content is determined by treating first with 91 per cent sulphuric acid, then distilling to remove any polymers, and finally by treating with 98 per cent acid.[45] The total loss sustained in these three steps is taken as the combined percentage of olefins and aromatics.

The aromatic content of the sample is then determined with a new sample from which the olefins are removed by treatment with sulphur monochloride.[46] The sample is subsequently distilled, first at atmospheric pressure, and then under reduced pressure. The products of the reaction between olefins and sulphur monochloride are probably dichlorosulphides or disulphides, which remain as a residue in the distillation flask provided the temperature of distillation is low. The distillate thus obtained contains 1 per cent or less of olefins, which can be estimated by titration with bromine. After determining the small quantity of olefins in the distillate the aromatic content is estimated by treating the sample with a nitrating mixture. The nitro-compounds thus formed are dissolved in either 95 or 91 per cent sulphuric acid, leaving a residue of unchanged hydrocarbons. The corrected loss in volume represents the aromatic content. With 95 per cent acid, a correction factor of 0.62 per cent is applied for the solution of non-aromatic constituents, whereas with 91 per cent acid the factor is 0.22 per cent. This method was later modified by Morrell and Levine[47] so that the olefin concentration could be calculated from the weight of residue remaining after distillation of the oil obtained upon treatment with 91 per cent acid by means of empirical formulas, as follows:

If U represents the actual olefin percentage; P, the weight of distillation residue; and D, the density of the oil remaining after the 98 per cent acid treatment; the following apply:

(1) For gasolines with a $\frac{P}{D}$ factor of 10 to 25 (15 to 25 per cent olefins)

$$U = 1.3\frac{P}{D} \quad \text{or} \quad U = \frac{P}{D} + 6$$

(2) For gasolines with a $\frac{P}{D}$ factor of 25 to 35 (35 to 50 per cent olefins)

$$U = 1.4\frac{P}{D} \quad \text{or} \quad U = \frac{P}{D} + 13$$

(3) For gasolines with a $\frac{P}{D}$ factor of 35 to 40 (50 to 60 per cent olefins)

$$U = 1.5\frac{P}{D} \quad \text{or} \quad U = \frac{P}{D} + L + 15$$

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[44] *Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 18.

[45] *Cf.* method described by Towne, *J. Inst. Pet. Tech.*, 1931, 17, 134; *Brit. Chem. Abs.* B, 1931, 469.

[46] Under the conditions prescribed by Faragher, Morrell and Levine, reactions between sulphur monochloride and both aromatics and paraffins are avoided. Lorand (*Ind. Eng. Chem.*, 1927, 19, 733) showed that sulphur monochloride reacts with the unsaturated hydrocarbons in petroleum distillates, and that this reaction formed the basis of a method for determining the comparative unsaturation of distillates.

[47] *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 321.

in which L = loss in volume per cent resulting after treatment with 98 per cent sulphuric acid subsequent to distillation.

Other methods proposed for the estimation of unsaturated hydrocarbons include the following: (1) Formation of addition compounds with perbenzoic acid[48] or camphoric acid peracid;[49] (2) reaction with liquid nitric oxide[50] at —15° to —20° C.; (3) reaction with ozone;[51] (4) reactions with hydrogen.[52]

ESTIMATION OF AROMATIC HYDROCARBONS BY ABSORPTION IN SULPHURIC ACID

The difficulties attending the use of sulphuric acid as a reagent for the separation and determination of unsaturated hydrocarbons have already been emphasized. With gasolines and light oils containing no unsaturated hydrocarbons, the determination of aromatics by absorption in sulphuric acid is a relatively simple matter. The only precaution to be observed is to make sure that the acid used does not attack any saturated hydrocarbons. As hydrocarbon analysis is usually conducted in such a way that unsaturated hydrocarbons are estimated and removed from the oil under test in the first step, it is convenient to limit this discussion to oils free from unsaturated hydrocarbons.

The aromatic hydrocarbons are readily attacked by concentrated sulphuric acid to form sulphonic acids, which remain dissolved in the acid. An approximate value of the aromatic content can be obtained by measuring the loss in volume of the gasoline or oil after this treatment. Kraemer and Böttcher[53] proposed shaking the gasoline with an equal volume of sulphuric acid containing 80 per cent by volume of concentrated acid and 20 per cent by volume of fuming acid. After allowing to stand for a short time, the decrease in volume of the gasoline is measured.

The quantity and concentration of sulphuric acid necessary to remove aromatic hydrocarbons completely and yet be without action on paraffin and naphthene hydrocarbons is controversial, although 98 per cent sulphuric acid has been used for this purpose by many investigators.[54] Sulphuric acid of strength 98 ± 1 per cent is used in the standard English procedure,[55] but other workers[56] state that 100 per cent sulphuric acid is necessary for the complete removal of aromatic hydrocarbons. Ormandy and Craven,[57] however, found that even 98 per cent sulphuric acid attacks hydrocarbons other than the aromatics, hence it is unsatisfactory for this separation.

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[48] Prileschaef, *J. Russ. Phys.-Chem. Soc.*, 1910, **42**, 1387; *Chem. Soc. Abs.*, 1911, **100** (1), 255; *J. Russ. Phys.-Chem. Soc.*, 1911, **43**, 609; *Chem. Soc. Abs.*, 1911, **100** (1), 604; *J. Russ. Phys.-Chem. Soc.*, 1912, **44**, 613; *Chem. Soc. Abs.*, 1912, **102** (1), 633; *Ber.*, 1909, **42**, 4811; *Chem. Abs.*, 1910, **4**, 916; Nametkin and Bryssova, *J. pr. Chem.*, 1926, **112**, 169; *Chem. Abs.*, 1926, **20**, 1397; Nametkin and Abakumovski, *J. pr. Chem.*, 1927, **115**, 56; *Chem. Abs.*, 1927, **21**, 1178; *Brit. Chem. Abs.* **B**, 1927, 179.

[49] Milas and Cliff, *J.A.C.S.*, 1933, **55**, 352.

[50] Smirnov, *Neft. Khoz.*, 1928, **15**, 217; *Chem. Abs.*, 1929, **23**, 965.

[51] Danaila, Andrei and Melinescu, *Bul. soc. Romana stiin*, 1923, **26** (4-6), 3; *Chem. Abs.*, 1924, **18**, 3710.

[52] See Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, **1930**; Skärblom, *Ted. Tik., Uppl. C. Kemi*, 1932, **62**, 57; *Chem. Abs.*, 1932, **26**, 5876; Waterman, van't Spijker, and van Westen, *Rec. trav. chim.*, 1929, **48**, 612, 1097, 1103, 1191; Waterman and van Westen, *Rec. trav. chim.*, 1929, **48**, 637, 1084.

[53] See Holde, "Untersuchung der Kohlenwasserstofföle und Fette," J. Springer, Berlin, **1913**, 62; *cf. Ber.*, 1887, **20**, 595; *Chem. Soc. Abs.*, 1887, **52**, 648; Engler-Höfer, "Das Erdöl," S. Hirzel, Leipzig, 1916, **4**, 21; *cf.* Worstall, *Amer. Chem. J.*, 1898, **20**, 664; Brooks and Humphrey, *J.A.C.S.*, 1918, **40**, 822.

[54] Morgan and Soule, *Ind. Eng. Chem.*, 1923, **15**, 587; Thole, *J.S.C.I.*, 1919, **28**, 39T; Tizard and Marshall, *ibid.*, 1921, **40**, 20T.

[55] "Standard Methods of Testing Petroleum and its Products," Institution of Petroleum Technologists, London, **1929**.

[56] Carpenter, *J. Inst. Pet. Tech.*, 1926, **12**, 518; *Chem. Abs.*, 1927, **21**, 1702; Hess, *Erdöl u. Teer*, 1926, **2**, 779; *Chem. Abs.*, 1927, **21**, 489; *Erdöl u. Teer*, 1927, **3**, 75; *Chem. Abs.*, 1927, **21**, 1346; Mühle and Dietrich, *Erdöl u. Teer*, 1926, **2**, 572; *Chem. Abs.*, 1926, **20**, 3560; Riesenfeld and Bandte, *Erdöl u. Teer*, 1926, **2**, 587; *Chem. Abs.*, 1926, **20**, 3801; *Erdöl u. Teer*, 1927, **3**, 139; *Chem. Abs.*, 1927, **21**, 1538; Winkler, *Przemysl Chem.*, 1930, **14**, 1; *Brit. Chem. Abs.* **B**, 1930, 272.

[57] *J. Inst. Pet. Tech.*, 1927, **13**, 311, 846; *Chem. Abs.*, 1927, **21**, 2554. *Cf.* Faragher, Morrell and Levine, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 18.

To outline this controversy a little further, the results of Manning,[58] Manning and Shepherd [59] and Kattwinkel [60] may be mentioned. Manning and Shepherd state that appreciable errors can arise from the solubility of the saturated hydrocarbons in the saturated solution of the sulphonated aromatic hydrocarbons. This is a point often ignored by other investigators. A mixture of aromatic-free petroleum ether and 20.0 per cent of benzene, for example, when shaken for ½ hour with 2 volumes of 98 per cent sulphuric acid, lost 17.0 per cent in volume, but the residual oil, on analysis, still contained 6.5 per cent of benzene. The acid therefore had dissolved 3.5 per cent of the petroleum ether. On shaking the same mixture for ½ hour with 3 volumes of 98 per cent acid, the loss in volume was 20 per cent but the residual oil still contained between 3 and 4 per cent of benzene. To effect complete removal of aromatic hydrocarbons, Manning and Shepherd proposed the use of 98 per cent sulphuric acid containing 2 to 3 per cent of silver sulphate. They assert that this substance greatly accelerates the sulphonation of benzene and its homologues but does not affect the action of the acid on saturated hydrocarbons. Kattwinkel,[61] on the other hand, recommended either sulphoacetic acid or the use of sulphuric acid (specific gravity, 1.84) containing 30 grams of phosphoric acid per 100 cc.

ESTIMATION OF AROMATIC HYDROCARBONS BASED ON SPECIFIC GRAVITY AND REFRACTION INDEX MEASUREMENTS

Because of the difficulties which exist in separating oils and sulphuric acid completely after acid treatment; numerous methods have been proposed in which the change in some physical property of the oil is used as an indication of the proportion of aromatic hydrocarbons absorbed by the acid. Such characteristics include the specific gravity, refractive index, and especially the critical solution temperatures of the oils in various solvents. The methods depend upon the fact that the aromatic hydrocarbons have higher specific gravities and refractive indices but lower critical solution temperatures than hydrocarbons of the other three classes.

Since aromatic hydrocarbons have higher specific gravities and refractive indices than other hydrocarbons, both these values decrease when aromatics are removed from a petroleum oil. A relationship exists between the aromatic content removed and the change in the physical property. Thus, the specific gravity and composition are related in the following way:

$$n = \frac{100\,D(d_1 - d_2)}{(D - d_2)\,d_1}$$

in which
n = Percentage of aromatics by weight
D = Specific gravity of aromatics only
d_1 = Specific gravity of oil under test
d_2 = Specific gravity of oil after extraction of aromatics

$$y = \frac{100\,(d_1 - d_2)}{D - d_2}$$

in which
y = Percentage of aromatics by volume, the other symbols having the same significance as above.

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[58] *J.C.S.*, 1929, 1014.

[59] *Dept. Sci. Ind. Res., Fuel Research Technical Paper* 28, 1930; *Brit. Chem. Abs.* B, 1931, 284; *Chem. Abs.*, 1931, 25, 396.

[60] *Chem. Ztg.*, 1925, 49, 57; *Chem. Abs.*, 1925, 19, 1113; *Brennstoff-Chem.*, 1927, 8, 353; *Chem Abs.*, 1928, 22, 3039.

[61] *Loc. cit.*

The estimation of aromatic hydrocarbons based on specific gravity measurements has been described by Thole.[62] In this method the light oil to be examined is divided into three fractions boiling at (1) 40° to 95° C., (2) 95° to 122° C., and (3) 122° to 150° C., it being assumed that these three fractions contain all the benzene, toluene and xylenes, respectively. Each fraction is sulphonated separately and the specific gravities of the oils remaining are determined. The aromatic content is calculated from this, assuming that the aromatic hydrocarbons in each fraction have the same specific gravity as benzene, toluene and xylene, respectively. The formulas given above are, however, only approximately correct, since some contraction in volume takes place when aromatic and non-aromatic hydrocarbons are mixed. Thole proposed corrections to compensate for the errors resulting from this phenomenon, but Tilitsheyev and Dumskaya[63] pointed out that these were not completely effective, because the errors depend to a considerable extent upon the chemical composition of the non-aromatic portion. Thus, when benzene is mixed with cyclohexane a greater reduction in volume occurs than when benzene is mixed with hexane. Tilitsheyev and Dumskaya compiled a series of tables showing the relationship between the specific gravity of the non-aromatic portion and the so-called aromatic coefficients, i.e., the variation in specific gravity produced by 1 per cent of aromatics. When corrections are made with these tables, the method is said to give accurate results for oils boiling below 150° C. Because the specific gravities of higher-boiling aromatics vary widely, the procedure is unreliable for oils boiling above 150° C.

A similar method in which the change in refractive index is observed has been proposed by Hoyte,[64] but this has been shown to be subject to the same limitations as the specific gravity method.[65] Determinations of refractive index have also been suggested by Lob[66] to give indications of the nature of the constituents of hydrocarbon mixtures.

ESTIMATION OF AROMATIC HYDROCARBONS BY MEASUREMENTS OF CRITICAL SOLUTION TEMPERATURES

Measurements of the temperature at which an oil and a liquid (solvent) become completely miscible afford a method for the analysis and examination of petroleum distillates. Such temperatures are known as critical solution temperatures (C.S.T.) and the methods based on their determination owe their significance to the fact that, of the various hydrocarbon classes, the aromatics have the lowest, and the paraffins the highest critical solution temperatures. The solvents used are chiefly aniline and nitrobenzene, although benzyl alcohol has also been suggested. In aniline, the critical solution temperature of normal heptane[67] is 70° C., that of cyclohexane[68] is 31° C., and that of trimethylethylene is 11° C. Benzene is completely miscible in aniline at —10° C. The critical solution temperature of a material furnishes, therefore, some information with regard to its chemical composition.

Chavanne and Simon[69] observed that the presence of aromatic hydrocarbons decreased the critical solution temperature of a hydrocarbon mixture in aniline and that the lowering was directly proportional to the weight of aromatics present. They suggested such measurements as a method of hydrocarbon analysis. Tizard and Marshall[70] established the proposed method on a sound experimental basis. The somewhat elaborate and time-consuming critical solution temperature measurements were replaced by the determinations of "Aniline Points," which may be defined as temperatures at which equal volumes of the hydrocarbon mixture and aniline become completely miscible. By this modification, the method was adapted to rapid manipulation without the loss of any of its accuracy. Tizard and Marshall found that benzene, toluene and ortho-xylene, in equal proportions by weight, produced the same depressions of the aniline point, within the limits of experimental error, but that meta- and para-xylenes lowered the aniline points rather less than the same weight of benzene and toluene. As an analytical procedure they proposed that the difference in aniline points of a gasoline be determined before and after sulphonation with 98 to 100 per cent sulphuric acid. The aromatic content corresponding to this difference is then read from a standard chart showing the relation between aromatic content and lowering of the aniline point.

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[62] *J.S.C.I.*, 1919, 38, 39T.
[63] *J. Inst. Pet. Tech.*, 1929, 15, 465; *Brit. Chem. Abs.* **B**, 1929, 879; *Chem. Abs.*, 1929, 23, 5566.
[64] *J. Inst. Pet. Tech.*, 1925, 11, 76; *Chem. Abs.*, 1925, 19, 1488.
[65] Ormandy and Craven, *J. Inst. Pet. Tech.*, 1926, 12, 68; *Chem. Abs.*, 1926, 20, 2581.
[66] *Z. angew. Chem.*, 1933, 46, 91; *Brit. Chem. Abs.* **B**, 1933, 293.
[67] Chavanne and Simon, *Compt. rend.*, 1919, 168, 1111; *Chem. Abs.*, 1919, 13, 2125; *Compt. rend.*, 1919, 168, 1324; *Chem. Abs.*, 1919, 13, 3182.
[68] Brame and Hunter, *J. Inst. Pet. Tech.*, 1927, 13, 794; *Brit. Chem. Abs.* **B**, 1928, 178.
[69] *Loc. cit.*

The general utility of aniline points in the examination of hydrocarbon oils was discussed by Brame and Hunter,[71] by Carpenter,[72] Minchin and Nixon,[73] and Robinzon.[74] Mizuta[75] observed that the aniline-point lowering for each per cent of aromatic hydrocarbon increases with the content of aromatic hydrocarbon, and shows a sudden change at 35 per cent. Thiophene had about 60 per cent of the aniline-point lowering of benzene.[76] Its influence on the determination of aromatics in straight-run gasoline is negligible. Tilitsheyev and Dumskaya[77] examined the method critically for mixtures of pure hydrocarbons and mixtures of pure hydrocarbons with light petroleum distillates. In attempting to apply the general equation,[78]

$$x = Kd$$

(in which x represents the percentage of aromatic hydrocarbons by weight, d is the difference in the aniline points before and after removal of the aromatics, and k is a coefficient), these investigators showed that the value of K is generally dependent upon the following factors:

(1) The nature of the aromatic hydrocarbons.
(2) Fractional composition of the gasoline.
(3) Chemical composition of the non-aromatic portion of the sample under investigation.
(4) Concentration of the aromatic hydrocarbons.

As a result of this, the aniline point method of analysis is best adapted to the examination of narrow fractions of hydrocarbon oils. This is especially true for oils boiling between 150° and 200° C., which give inaccurate results by the specific gravity and refractive index methods.

The value to be given to the coefficient K must be carefully ascertained by trial experiments with the particular aromatic hydrocarbons which are to be estimated. If the nature of these hydrocarbons is unknown, the value of K may be assumed to be 1.2, but it must be realized that in some cases, depending upon the nature of the aromatic hydrocarbons and also of the non-aromatic components, the true value may be as high as 2.0 or as low as 1.0.

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[70] *J.S.C.I.*, 1921, **40**, 20T.

[71] *J. Inst. Pet. Tech.*, 1927, **13**, 794; *Brit. Chem. Abs.* **B**, 1928, 178.

[72] *J. Inst. Pet. Tech.*, 1926, **12**, 562; *Brit. Chem. Abs.* **B**, 1927, 673. *J. Inst. Pet. Tech.*, 1928, **14**, 446; *Brit. Chem. Abs.* **B**, 1928, 736.

[73] *J. Inst. Pet. Tech.*, 1928, **14**, 477; *Brit. Chem. Abs.* **B**, 1928, 699.

[74] *Neft. Khoz.*, 1932, **22**, 226; *Chem. Abs.*, 1932, **26**, 4453.

[75] *J. Soc. Chem. Ind., Japan*, 1931, **34**, 407B, 489B; *Brit. Chem. Abs.* **B**, 1932, 168, 297.

[76] Mizuta, *J. Soc. Chem. Ind., Japan*, 1932, **35**, 43B; *Brit. Chem. Abs.* **B**, 1932, 375.

[77] *J. Inst. Pet. Tech.*, 1929, **15**, 465; *Brit. Chem. Abs.* **B**, 1929, 879; *Chem. Abs.*, 1929, **23**, 5566.

[78] This equation is applicable to other methods, such as those depending upon the difference in specific gravity or refractive index of the sample before and after removal of aromatics. The numerical value of K, of course, depends upon the particular method employed.

It is essential, in order to obtain accurate results, that the aniline used be absolutely dry and pure, and for this reason it should be freshly distilled. The presence of 1 per cent of water raises the aniline point of normal heptane[79] by 6.2° C. It is best to standardize the aniline against a hydrocarbon of known purity—normal heptane appears to be the most convenient hydrocarbon for this purpose, as it may easily be obtained of 99.9 per cent purity from the oil of *Pinus sabiniana.*[80] Table 161, mainly from data collected by Howes,[81] gives the aniline points of certain pure hydrocarbons and shows that

(1) The aniline points of hydrocarbons of a homologous series increase as the boiling points of the hydrocarbons increase.
(2) The aniline points of isoparaffins and iso-olefins are higher than those of their normal homologues.
(3) The aniline points of the naphthenes are lower than those of the paraffins, ranging from 20° to 60° C.

The measurement of aniline points has been proposed by Ormandy and Craven[82] and by Tizard and Marshall[83] as the basis of a method for the estimation of naphthene hydrocarbons in naphthene-paraffin mixtures, in which the following assumptions are made:

(1) That all paraffin hydrocarbons have an aniline point of 70° C.
(2) That all naphthene hydrocarbons boiling up to 95° C. lower the aniline points of paraffins by 0.4° C.; all naphthenes boiling between 95° and 120° C., by 0.3° C.; and all naphthenes boiling above 120° C., by 0.2° C. for each per cent of naphthene. In practice the average figure of 0.3° C. is used. If N = per cent naphthenes, and T = aniline point of the paraffin-naphthene mixture, the value of N may be calculated, therefore, as follows:

$$N = \frac{70 - T}{0.3}$$

This method gives inaccurate results because of the assumptions on which it is founded. Garner[84] described a somewhat similar method of estimating naphthene hydrocarbons in such mixtures, in which allowance is made for the rise of aniline point with increase in boiling point. The Garner method gives more accurate results than that of Ormandy and Craven.

Schaarschmidt, Hofmeier and Leist[85] used aniline points for the determination of the naphthene and paraffin content of mixtures. The naphthene content (N) can be calculated from the formula:

$$N = \frac{A - A_m}{A - a}$$

in which A = aniline point of component having the higher aniline point; A_m = aniline point of the mixture; a = aniline point of other component.

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[79] Ormandy and Craven, *J. Inst. Pet. Tech.*, 1926, 12, 89; *Chem. Abs.*, 1926, 20, 2581.

[80] Wenzel, *Pharm. J.*, March 30, 1872; Thorpe, *J.C.S.*, 1879, 35, 296; Brame and Hunter, *J. Inst. Pet. Tech.*, 1927, 13, 794; *Brit. Chem. Abs.* B, 1928, 178.

[81] *J. Inst. Pet. Tech.*, 1930, 16, 54; *Brit. Chem. Abs.* B, 1930, 802.

[82] *J. Inst. Pet. Tech.*, 1924, 10, 101; *Chem. Abs.*, 1924, 18, 1744.

[83] *J.S.C.I.*, 1921, 40, 20T.

[84] *J. Inst. Pet. Tech.*, 1928, 14, 695; *Brit. Chem. Abs.* B, 1929, 84.

[85] *Z. angew. Chem.*, 1930, 43, 954; *Chem. Abs.*, 1931, 25, 1064.

TABLE 161.—*Aniline Points of Pure Hydrocarbons.*

Paraffin Hydrocarbons

Pentanes

n-Pentane 72° C.[a]
2-Methylbutane 77° C.[b]

Hexanes

n-Hexane 69° C.[a]
2-Methylpentane 73.8° C.[a]
74.7° C.[b]
3-Methylpentane 69.4° C.[b]
2,2-Dimethylbutane 80.75° C.[b]
2,3-Dimethylbutane 72.3° C.[b]

Heptanes

n-Heptane 68° C.[e]
70° C.[a d]
71° C.[e]
2-Methylhexane 72.8° C.[a e]
3-Ethylpentane 66.3° C.[d]
2,2-Dimethylpentane 77.7° C.[d]
2,3-Dimethylpentane 68.1° C.[d c]
2,4-Dimethylpentane 78.8° C.[d]
3,3-Dimethylpentane 71.0° C.[d]
2,2,3-Trimethylbutane 72.4° C.[d]

Higher Paraffins

n-Octane 71.8° C.[a]
n-Nonane 74.5° C.[e]
n-Decane 77.5° C.[e]
n-Undecane 77.78° C.[f]

Naphthene Hydrocarbons

Cyclopentane 18° C.[a]
Methylcyclopentane 35° C.[a]
Ethylcyclopentane 39° C.[g]
Propylcyclopentane 45° C.[g]
Butylcyclopentane 50.5° C.[g]
1,3-Dimethylcyclopentane 45° C.[a]
1,2,3-Trimethylcyclopentane 41° C.[e]
Cyclohexane 31° C.[a]
Methylcyclohexane 41° C.[a]
1,2-Dimethylcyclohexane 42.1° C.[a]
1,3-Dimethylcyclohexane 49.7° C.[a]
1,4-Dimethylcyclohexane 48.0° C.[a]
1,2,3-Trimethylcyclohexane 53.6° C.[e]
1-Methyl-4-isopropylcyclohexane 56.5° C.[e]

Bicyclic Hydrocarbons

Decahydronaphthalene 34° C.[e]
Tetrahydronaphthalene 20° C.[e]
Cyclohexylcyclohexane 12° C.[e]
Methylcyclohexylcyclohexane 15° C.[e]

Olefin Hydrocarbons

1-Pentene 19.3° C.[h]
1-Hexene 22.9° C.[h]
1-Heptene 26.6° C.[h]
1-Octene 32.8° C.[h]
1-Nonene 38.6° C.[h]
Isohexene 24° C.[e]
Cyclohexene 20° C.[a]
Amylene 14.5° C.[i]
Trimethylethylene 11.0° C.[j]
10.0° C.[e]
2-Pentene 18° C.[e]
Hexene 17° C.[e]
Heptene 36° C.[e]
Octene 26.5° C.[e]
Cetene 68° C.[e]

[a] Chavanne and Simon, *Compt. rend.*, 1919, **168**, 1111; *Chem. Abs.*, 1919, **13**, 2125; *Compt. rend.*, 1919, **168**, 1324; *Chem. Abs.*, 1919, **13**, 3182.
[b] Chavanne, *Bull. soc. chim. Belg.*, 1922, **31**, 331; *Chem. Abs.*, 1923, **17**, 2777.
[c] Ormandy and Craven, *J. Inst. Pet. Tech.*, 1926, **12**, 89; *Chem. Abs.*, 1926, **20**, 2581.
[d] Edgar, Calingaert and Marker, *J.A.C.S.*, 1929, **51**, 1483.
[e] Garner, *J. Inst. Pet. Tech.*, 1928, **14**, 713; *Chem. Abs.*, 1929, **23**, 964.
[f] Carpenter, *J. Inst. Pet. Tech.*, 1926, **12**, 562; *Chem. Abs.*, 1927, **21**, 1702.
[g] Chavanne, *Bull. sci. acad. roy. Belg.*, 1926, (5) **12**, 105; *Chem. Abs.*, 1926, **20**, 2664.
[h] Wilkinson, *J.C.S.*, 1931, 3057.
[i] Konowalow, *Ann. Phys.*, 1903, 375.
[j] Brame and Hunter, *J. Inst. Pet. Tech.*, 1927, **13**, 794; *Chem. Abs.*, 1928, **22**, 2832.

Nitrobenzene has also been suggested as a liquid to employ in critical solution temperature determinations. It is said to have certain advantages over aniline when used for this purpose. As with the latter solvent, the presence of aromatics lowers the critical solution temperature of mixtures of hydrocarbons and nitrobenzene. A sufficiently linear relationship exists between the C.S.T. depression and the amount of aromatics added to allow nitrobenzene to be used in this way. Erskine[86] found that the values of K in the general equation: $x = KT$ are 0.845 for benzene, 0.890 for toluene, and 0.938 for xylene, when equal weights of hydrocarbon mixtures and nitrobenzene are employed. Compared with those obtained with mixtures of hydrocarbons and aniline, the C.S.T.'s of mixtures of hydrocarbons and nitrobenzene are much lower, and the C.S.T.'s of mixtures of normal paraffin hydrocarbons and nitrobenzene decrease with increasing molecular weight and boiling point. See Table 162.

TABLE 162.—*Critical Solution Temperature of Paraffins in Nitrobenzene.*

	° C.
n-Pentane	24.5
Isopentane	31.25
n-Hexane	14.8
Isohexane	24.05
n-Heptane	11.5
Isoheptane	18.05

The use of the critical solution temperature in nitrobenzene for the estimation of aromatics has been examined by Dobryanskii and Khesin,[87] who found that the value of the coefficient K falls off rather rapidly with increase in concentration of the aromatics but that it has practically the same value for all aromatic hydrocarbons with short side-chains. Tilitsheyev and Dumskaya[88] compared the aniline and nitrobenzene methods and found that the latter has the following advantages:

1. Lower critical solution temperatures and therefore more rapid determination.
2. Smaller fluctuations of nitrobenzene coefficient as a result of variation of the chemical composition of the non-aromatic portion.
3. Greater stability of nitrobenzene.

The nitrobenzene method is especially adapted to the examination of very light and volatile hydrocarbons, because the lower critical solution temperatures minimize the danger of loss by evaporation.

All methods for estimating aromatic hydrocarbons by C.S.T. measurements before and after the removal of aromatics are dependent for their accuracy upon the efficiency of the reagent used to extract the aromatics. If the reagent removes these hydrocarbons incompletely, the estimated aromatic content will be too low and the estimated naphthene content (if this, too, is determined by C.S.T. measurements) will be too high. To overcome this difficulty, Aubert and Aubrée[89] developed a procedure in which the removal of aromatic hydrocarbons is unnecessary. The method is applicable only to ternary mixtures and was suggested particularly for the analysis of aviation gasoline. It was tested with mixtures of pure hexane, heptane, octane, decane, cyclohexane, methylcyclopentane, benzene and toluene.

The basis of this method is as follows:

If $T =$ C.S.T. of original mixture
$T_1 =$ C.S.T. of mixture after removal of aromatics
$\theta_n =$ C.S.T. of naphthenes
$\theta_p =$ C.S.T. of paraffins
$A =$ per cent aromatics
$N =$ per cent naphthenes
$P =$ per cent paraffins

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[86] *Ind. Eng. Chem.*, 1926, 18, 694.
[87] *Azerb. Neft. Khoz.*, 1929, No. 8-9, 80; *Chem. Abs.*, 1930, 24, 952.
[88] *J. Inst. Pet. Tech.*, 1929, 15, 465; *Brit. Chem. Abs.* B, 1929, 879; *Chem. Abs.*, 1929, 23, 5566.
[89] *Compt. rend.*, 1926, 182, 577; *Chem. Abs.*, 1926, 20, 1712.

Then

$$A = K(T_1 - T)$$

and

$$N = \frac{\theta_p - T_1}{\theta_p - \theta_n}(100 - A)$$

and by eliminating T_1 between the two equations

$$\frac{N(\theta_p - \theta_n)}{100 - A} = \theta_p - \left(\frac{A}{K} + T\right)$$

a relationship which does not involve T_1.

It is necessary to use two solvents for both of which the general values of K, θ_n and θ_p are known. The critical solution temperature of the mixture in each of these solvents is then determined, and after substituting the appropriate values in the above formula, two equations with two unknown quantities (A and N) are obtained. From these equations the values of A and N can be determined. Aniline is used as one solvent for the C.S.T. determinations and benzyl alcohol, because of its high boiling point (206° C.), was suggested as the other solvent.

Aromatics are soluble in all proportions in benzyl alcohol at ordinary temperatures, and the critical solution temperatures of hydrocarbons in benzyl alcohol are lower than in aniline, which is especially favorable for the examination of volatile fractions. For the two saturated series of hydrocarbons, namely, naphthenes and paraffins, the variation in C.S.T. from one member to another of the same series is more accentuated than with aniline.[90] This makes the use of benzyl alcohol not as well adapted to approximate analyses of gasolines and light oils as to the precise analyses of narrow fractions. In view of the fact that unsaturated hydrocarbons also have low aniline points, their presence will materially affect the accuracy of any results obtained in the determination of aromatics. It is therefore necessary to remove unsaturated hydrocarbons completely before an estimation of aromatics is conducted in this way. According to Garner,[91] a given weight of unsaturated hydrocarbons depresses the aniline point of a hydrocarbon mixture to two-fifths the extent produced by the same weight of aromatics. This, however, is to be considered only as an approximate figure. Dietrich[92] suggested the determination of aromatics by critical solution temperatures of 7 parts of the oil with 3 parts of 96 per cent ethyl alcohol. The critical solution temperatures of hydrocarbon mixtures containing over 50 per cent aromatics cannot be determined with aniline because of the low temperature. Liquid ammonia has been suggested as the solvent for such mixtures by Tropsch and Simek.[93]

ESTIMATION OF AROMATIC HYDROCARBONS WITH NITRIC ACID AND NITRIC-SULPHURIC ACID MIXTURES

The ease with which aromatic hydrocarbons may be nitrated has led to the development of other methods for the estimation of these substances. In a procedure of this kind, the aromatics are treated with fuming nitric acid. The nitrated products are then dissolved in a known volume of sulphuric acid. From the increase in volume of the acid layer,[94] the content of aromatic hydrocarbons may be calculated. This method, however, is not accurate because a change in volume occurs when nitrated products are dissolved in sulphuric acid, and each nitrated hydrocarbon not only gives a different volume change but also a different volume of nitrated products. For similar reasons, methods based on the weight of nitro-compounds produced are also inaccurate. Such methods have been proposed by Florentin and Vandenberghe,[95] and Heyn and Dunkel.[96] A more accurate procedure is to measure the volume of unchanged saturated hydrocarbons after treatment. This is recommended by Hess.[97] Egloff and Morrell[98] proposed a method depending upon the use of a concentration of nitric-sulphuric acid (25% nitric acid, 58% sulphuric acid, 17% water) in which nitro-aromatic bodies are not soluble, but separate out as a distinct layer whose volume can be measured. The volume of this layer is multiplied by a constant (4.3) to convert it directly to percentage aromatics. According to Riesenfeld and Bandte,[99] the method recommended by Hess gives good results, but those obtained by the Egloff and Morrell method are too low for mixtures of low aromatic content and too high for mixtures of high aromatic content. The latter observation was confirmed by Faragher, Morrell and Levine.[100] Garner[101] used fuming nitric acid at temperatures of —10° to —15° C. to remove both aromatic and unsaturated hydrocarbons. Accordingly, the gasoline is shaken with fuming acid at the temperature mentioned and the nitro-bodies which dissolve in the residual gasoline are washed out with additional fuming nitric acid. From the difference in the aniline points of the gasoline before and after treatment, is obtained the "aromatic equivalent", i.e., the percentage of aromatic hydrocarbons which correspond to such a lowering.[102] The percentage loss in volume resulting after the nitric acid treatment is also determined. From these two values (assuming that unsaturated hydrocarbons depress aniline points to two-fifths the same extent as aromatic hydrocarbons, as previously mentioned), the percentage of each type of hydrocarbon can be calculated in the following manner:

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[90] Aubrée, *Chimie et industrie*, Spec. No., Sept. 1926, 336; *Chem. Abs.*, 1927, 21, 644.
[91] *J. Inst. Pet. Tech.*, 1928, 14, 695; *Brit. Chem. Abs.* **B**, 1929, 84.
[92] *Autotechnik*, 1927, 16, 7; *Brit. Chem. Abs.* **B**, 1928, 882.
[93] *Mitt. Kohlenforschungsinst. Prag*, 1931, 62; *Brit. Chem. Abs.* **B**, 1933, 497.
[94] Halphen, *Mat. grasses*, 1911, 3, 1987; *Chem. Abs.*, 1911, 5, 1676.

If $A =$ per cent aromatics
$B =$ per cent unsaturates
$a =$ aromatic equivalent
$b =$ percentage loss in volume after nitric acid treatment

then

$$A + \frac{2}{5}B = a$$

$$A + B = b$$

or

$$B = \frac{5}{3}(b - a) \quad \text{and} \quad A = b - B.$$

Another method for the determination of aromatics has been described by Manning.[103] A small sample of the oil is weighed into a small U-tube and vaporized by drawing through it a current of nitrogen or carbon dioxide-free air. If unsaturated hydrocarbons are absent, the oil vapors are absorbed in 98 per cent sulphuric acid (also in a U-tube) containing 2 to 3 per cent silver sulphate. The gain in weight of the tube represents the aromatic content of the sample.

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[95] *Bull. soc. chim.*, 1920, **27**, 204; *J.S.C.I.*, 1920, **39**, 325A.

[96] *Brennstoff-Chem.*, 1926, **7**, 245; *Chem. Abs.*, 1927, **21**, 640.

[97] *Z. angew. Chem.*, 1920, **33** (1), 147; *J.S.C.I.*, 1920, **39**, 509A.

[98] *Ind. Eng. Chem.*, 1926, **18**, 354. *Cf.* Tarassov, *Neft. Khoz.*, 1926, **11**, 67; *Chem. Abs.*, 1928; **22**, 3285.

[99] *Erdöl u. Teer*, 1926, **2**, 491; *Chem. Abs.*, 1926, **20**, 3346.

[100] *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 18.

[101] *J. Inst. Pet. Tech.*, 1928, **14**, 695; *Brit. Chem. Abs.* **B**. 1929, 84.

[102] This value is actually calculated from the data previously given by Tizard and Marshall.

[103] *J.C.S.*, 1929, 1014.

When the sample contains unsaturated hydrocarbons, the oil vapors are absorbed in a nitrating mixture (10 per cent concentrated nitric acid, or 16 per cent potassium nitrate in concentrated sulphuric acid) contained in small potash bulbs. The increase in weight of the bulbs corresponds to the aromatic and unsaturated content of the oil, after a small correction has been applied for the retention of saturated hydrocarbon vapors. The nitration of the aromatics is completed by adding a little more nitric acid and heating for 2 to 3 hours on a water bath. The unsaturated hydrocarbons are at the same time oxidized to carbon dioxide, acids and other compounds soluble in water and aqueous alkali solution. The nitration mixture is poured into water, the nitrated products are extracted with benzene and, after washing, the benzene is evaporated. From the weight of products obtained, the percentage of aromatics is calculated by multiplying by the factor 0.452.

DETERMINATION OF AROMATIC HYDROCARBONS BY THE USE OF PREFERENTIAL SOLVENTS

As mentioned in Chapter 1, the most widely used solvent for the extraction of aromatics from petroleum distillates is liquid sulphur dioxide, which was originally suggested by Edeleanu[104] and which is used in the commercial refining of lubricating oils and for the removal of aromatics from kerosene. Laboratory tests on the extraction of aromatics with liquid sulphur dioxide have been carried out by Moore, Morrell and Egloff.[105] Another well-known solvent for aromatic hydrocarbons is dimethyl sulphate, proposed by Valenta,[106] who stated that it has no solvent action on paraffins or naphthenes. This assertion has been refuted by others.[107]

Various other solvents have been suggested, including aniline,[108] diethyl sulphate,[109] levulic acid, phenylhydrazine, glycol monoacetate, and furfuraldehyde,[110] and sulphoacetic acid[111] in acetic anhydride. However, none of these give accurate results because the solubility of the different classes of hydrocarbons in each other is far greater than the solubility in any solvent.

ESTIMATION OF PARAFFIN AND NAPHTHENE HYDROCARBONS

In the analysis of a light mineral oil, after unsaturated and aromatic hydrocarbons have been removed, a mixture of paraffins and naphthenes remains. The estimation of these two classes of hydrocarbons in the presence of each other is a difficult task. The only methods which give even approximately accurate results are those described by Tizard and Marshall,[112] Ormandy and Craven,[113] Garner,[114] and Schaarschmidt, Hofmeier, and Leist.[115]

Other procedures, however, have been suggested. Danaila, Andrei and Melinescu[116] proposed that the cyclohexane series of naphthenes be estimated by dehydrogenation over a nickel catalyst at an appropriate temperature. In this way, the naphthene hydrocarbons are converted into aromatics, which may be estimated by sulphonation in the manner already described. Obviously the cyclopentanes cannot be estimated in this manner. A similar dehydrogenation, in which palladium black was the catalyst, has been used by Manning and Shepherd.[117] At a temperature of 350° C. in a current of nitrogen, a 94 per cent conversion of cyclohexane into benzene resulted, but attempts to dehydrogenate cyclohexane mixed with petroleum ether (boiling point, 40° to 60° C.) failed. The results were low and could not be duplicated. Moreover, no further dehydrogenation was effected by recirculation of the vapor over the catalyst. Not only were the paraffin hydrocarbons decomposed to some extent but the unsaturated residues appeared to have coupled with the partly dehydrogenated cyclohexane to form higher homologues of the latter, which were not completely dehydrogenated under the conditions employed. These difficulties were overcome by working at a slightly lower temperature (320° to 335° C.), at which the higher homologues of cyclohexane were not as readily dehydrogenated as cyclohexane itself. In nitrogen at 350° to 360° C., not more than 70 per cent of methylcyclohexane was converted, whereas in hydrogen only 38 per cent was dehydrogenated. The equilibrium point of the reaction, which for cyclohexane corresponds to almost complete dehydrogenation under the experimental conditions employed, corresponds to only a partial dehydrogenation for methylcyclohexane. By working at 330° C. and removing the toluene as formed, 93 to 96 per cent conversion was obtained.

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[104] *J. Inst. Pet. Tech.*, 1932, **18**, 900; see Kalichevsky and Stagner, "Chemical Refining of Petroleum," Chemical Catalog Co., Inc., New York, 1933, 220.

[105] *Chem. Met. Eng.*, 1918, **18**, 396; *Chem. Abs.*, 1918, **12**, 1923.

[106] *J. Inst. Pet. Tech.*, 1928, **14**, 695; *Brit. Chem. Abs.* **B**, 1929, 84.

[107] Graefe, *Rev. Fett-Harz-Ind.*, 1907, **14**, 112; *Chem. Abs.*, 1907, **1**, 1909; Spausta, *Petroleum Z.*, 1931, **27**, 765; *Brit. Chem. Abs.* **B**, 1932, 8; Harrison and Perkin, *Analyst*, 1906, **31**, 202; *ibid.*, 1908, **33**, 2; *Chem. Soc. Abs.*, 1908, **94** (2), 135.

[108] Heilingötter, *Allgem. Oel- u. Fett-Ztg.*, 1932, **29**, 377; *Chem. Abs.*, 1933, **27**, 2278.

[109] Taylor, *Ind. Eng. Chem.*, 1927, **19**, 76.

[110] Göhre, *Petroleum Z.*, 1927, **23**, 73; *Brit. Chem. Abs.* **B**, 1927, 131.

[111] Kattwinkel, *Chem. Ztg.*, 1925, **49**, 57; *J.S.C.I.*, 1925, 616B.

[112] *J.S.C.I.*, 1921, **40**, 20T.

[113] *J. Inst. Pet. Tech.*, 1924, **10**, 101; *Chem. Abs.*, 1924, **18**, 1744.

[114] *J. Inst. Pet. Tech.*, 1928, **14**, 695; *Brit. Chem. Abs.* **B**, 1929, 84.

[115] *Z. angew. Chem.*, 1930, **43**, 954; *Chem. Abs.*, 1931, **25**, 1064.

SEPARATION OF UNSATURATED HYDROCARBONS FROM PETROLEUM

The analytical methods already described in this chapter for the estimation of the classes of hydrocarbons in the lighter distillates of petroleum are of little value for the isolation of these substances. Other means must be employed for this purpose. In work of this character, the use of distillation columns similar to those described by investigators at the U. S. Bureau of Standards[118] offer many advantages. These columns are of the bubble-plate variety and give extremely efficient fractionation.

Hydrocarbons of the olefin series may be separated conveniently from other hydrocarbons as dibromides. The bromine addition products are of high boiling point and may be fractionated from unchanged hydrocarbons. Subsequently, they may be decomposed by the action of a zinc-copper couple and alcohol (Gladstone and Tribe's method[119]) to give the parent olefins. In the bromination of olefins, the temperature should not rise above —5° C., otherwise substitution may occur. A convenient method to adopt for the decomposition of the dibromides is to cover a freshly prepared zinc-copper couple with 90 per cent ethyl alcohol, gently boil the alcohol and gradually add to it the dibromide. The heat of reaction is generally sufficient (in the case of the lower hydrocarbons) to distil the olefin as liberated, but with higher olefins, heat from an outside source may be necessary. The alcohol-olefin distillate may be diluted with water, the olefins separated, dried and fractionated. On the other hand, it may be found convenient to fractionate the dibromides before decomposition, usually under reduced pressure. This method of isolating olefin hydrocarbons has been used successfully by Brame and Hunter,[120] and by Wilkinson.[121]

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[116] *Bul. soc. Romana stiin.*, 1923, **26** (4-6), 2; *J.S.C.I.*, 1924, **43**, 857B; see also Danaila and Stoenescu, *Petroleum Z.*, 1927, **23**, 107; *Bul. soc. Romana stiin.*, 1926, **29**, 23; *Chem. Abs.*, 1927, **21**, 2787.

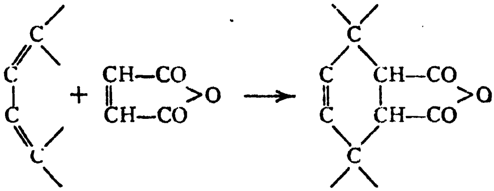
[117] *Dept. Sci. Ind. Res., Fuel Research Technical Paper* **28**, 1930; *Brit. Chem. Abs.* **B**, 1931, 284; *Chem. Abs.*, 1931, **25**, 396.

[118] Bruun, *Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 212. Washburn, Bruun and Hicks, *Bur. Standards J. Research*, 1929, **2**, 470; *Chem. Abs.*, 1929, **23**, 2279.

[119] *J.C.S.*, 1878, **33**, 306.

The same general procedure may be used for the isolation of diolefins. The diolefin tetrabromides which form can be separated from the dibromides resulting from monolefins, by fractionation. Butadiene and piperylene give solid tetrabromides, whereas isoprene, cyclopentadiene and the dimethyl butadienes yield liquid tetrabromides (see Chapter 27).

Cyclopentadiene has been isolated from oil-gas condensate by Etard and Lambert[122] and from lignite-tar and coal-tar oils by Krämer and Spilker[123] as the dimer, which readily forms on standing and can be decomposed by distillation. This method, involving polymerization and subsequent depolymerization, is only of use with certain cyclic diolefins. For the identification of diolefins, the typical reaction (described in Chapter 27) between diolefins and maleic anhydride may be used. This reaction proceeds as follows:



and the products formed are characteristic crystalline derivatives.[124]

As already mentioned, attempts have been made by Brame and Hunter[125] to use the reaction between olefins and mercuric acetate for the isolation of unsaturated hydrocarbons. Unfortunately, large amounts of hydrocarbons were destroyed and lost when the resulting complexes were decomposed with acids.

Separation of Aromatic Hydrocarbons from Petroleum

Because aromatic hydrocarbons have lower critical solution temperatures in aniline than other hydrocarbons, it has been found convenient to use methods of preferential extraction with such solvents to obtain oil fractions rich in aromatics. In this way a partial concentration of aromatic hydrocarbons can be effected. From such a concentrate the individual hydrocarbons can be separated by chemical methods. Solvents commonly used for such fractional extractions are aniline and liquid sulphur dioxide and the operations are usually conducted at a temperature of 0° C. or lower.

Such procedures have been used by Bruun and Hicks-Bruun[126] for the isolation of benzene from an Oklahoma crude oil and proved valuable in the separation of benzene from constant-boiling mixtures of benzene and hexanes which could not be resolved readily by other means. Thus 1600 volumes of a 68°-69° C. fraction (n^{20}_{D} 1.395) was extracted once with aniline in a special apparatus designed for this purpose. As a result two fractions were obtained, one of 200 volumes with n^{20}_{D} 1.419 and the other of 1300 volumes with n^{20}_{D} 1.391. By subjecting the 200-volume fraction to fractional crystallization a sample of purified benzene (n^{20}_{D} 1.501) was obtained.[127] An apparatus used by Bruun and Hicks-Bruun[128] permits the solvent extraction to be made conveniently more than once, the extent of the separation increasing, of course, with each extraction.

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[120] *J. Inst. Pet. Tech.*, 1927, 13, 794; *Brit. Chem. Abs.* B, 1928, 178.
[121] *J.C.S.*, 1931, 3057.
[122] *Compt. rend.*, 1891, 112, 945; *J.S.C.I.*, 1891, 10, 688.
[123] *Ber.*, 1896, 29, 553; *J.S.C.I.*, 1896, 15, 443.
[124] Birch and Scott, *Ind. Eng. Chem.*, 1932, 24, 49.
[125] *J. Inst. Pet. Tech.*, 1927, 13, 794; *Brit. Chem. Abs.* B, 1928, 178.
[126] *Bur. Standards J. Research*, 1931, 6, 869; *Chem. Abs.*, 1931, 25, 4111.

Carpenter[129] pointed out that aniline containing a small proportion of water has a more selective action on hydrocarbons than dry aniline. Low temperatures were also found to be of advantage. Such methods of preferential extraction with solvents may be employed for the partial separation of naphthene hydrocarbons from paraffins.

Another method used for the extraction and isolation of aromatic hydrocarbons from light petroleum distillates is that of Armstrong and Miller,[130] in which aromatic sulphonic acids are decomposed to the original hydrocarbons with superheated steam. When this procedure is employed, the oil can be sulphonated with 98 per cent sulphuric acid. The sulphuric acid containing the sulphonated products can then be treated as mentioned. This method has been used by Mulany and Watson[131] in a study of the aromatic content of Burmah light oils and by Iimori and Kikuchi.[132] Carpenter,[133] however, obtained only a yield of 60 per cent of the aromatics originally present in a Burmah crude.

SEPARATION OF PARAFFIN HYDROCARBONS FROM PETROLEUM

Paraffin hydrocarbons, because they are more stable than other hydrocarbons, can be separated from aromatics, olefins and naphthenes by treating mixtures containing them with reagents which react with the other three classes of hydrocarbons. Such processes, however, only yield the normal paraffins, because the branched-chain isomers are also attacked. A reagent suggested for this purpose is chlorosulphonic acid, which has been used by Shepard and Henne,[134] Shepard, Henne and Midgley,[135] Leslie and Schicktanz,[136] and by Bruun and Hicks-Bruun.[137] According to Shepard and Henne, paraffin and naphthene hydrocarbons containing secondary and tertiary carbon atoms are rapidly attacked by this reagent, whereas the normal paraffin hydrocarbons and cyclohexane and cyclopentane are only slowly affected. The latter hydrocarbons may be separated by fractional distillation. Unfortunately, the reaction takes a long time to reach completion. Shepard and Henne found it necessary to subject a decane fraction to this treatment for a period of 37 days to purify it.

Another reagent which has been used for the separation of branched-chain hydrocarbons from hydrocarbon mixtures is antimony pentachloride. Schaarschmidt[138] found that treatment with this substance caused the separation of tertiary compounds as an oily or crystalline mass which assumed an intense violet color when shaken with alcohol. One molecule of the hydrocarbon appears to react with two of antimony pentachloride. Normal and quaternary compounds also react but heat is required.

[127] Washburn, Bruun and Hicks, *Bur. Standards J. Research,* 1929, **2**, 484; *Chem. Abs.,* 1929, **23**, 2279.

[128] *Loc. cit.*

[129] *J. Inst. Pet. Tech.,* 1928, **14**, 446; *Chem. Abs.,* 1928, **22**, 3766.

[130] *J.C.S.,* 1884, **45**, 148; *ibid.,* 1886, **49**, 74.

[131] *J.S.C.I.,* 1924, **43**, 310T; *J.S.C.I.,* 1924, **43**, 1002B.

[132] *Bull. Inst. Phys. Chem. Res. Tokyo,* 1929, **8**, 984; *Brit. Chem. Abs.* **B**, 1930, 272.

[133] *J. Inst. Pet. Tech.,* 1926, **12**, 518; *Brit. Chem. Abs.* **B**, 1927, 673.

[134] *Ind. Eng. Chem.,* 1930, **22**, 356.

[135] *J.A.C.S.,* 1931, **53**, 1948.

[136] *Bur. Standards J. Research,* 1931, **6**, 377; *Chem. Abs.,* 1931, **25**, 2551.

[137] *Bur. Standards J. Research,* 1931, **6**, 869; *Chem. Abs.,* 1931, **25**, 4111.

[138] *Z. angew. Chem.,* 1931, 474; *Petroleum Z.,* 1932, **28** (12), 1; *Chem. Abs.,* 1932, **26**, 4706; *Brit. Chem. Abs.* **B**, 1932, 493.

The formation of constant-boiling mixtures with methyl alcohol has been used by Bruun and Hicks-Bruun[139] in the isolation of isomeric hexanes from an Oklahoma crude oil and in the isolation of cyclohexane[140] and methylcyclopentane.[141] Fractional crystallization has been used in the isolation of pure paraffins and other hydrocarbons,[142] for example, in the separation of n-octane from an Oklahoma crude oil.[143] It was shown to be a good method for the resolution of azeotropic mixtures which cannot be separated conveniently by other means.

DISTILLATION TESTS

For routine testing of petroleum and its fractions various methods have been standardized by the American Society of Testing Materials (A.S.T.M.) and The Institution of Petroleum Technologists (I.P.T.). These methods are, for the most part, concerned with the determination of characteristics which decide the market values of the oils. These methods have been in general use in the petroleum industry for extensive periods and considerable information has been obtained with regard to their significance.[144] The following account is intended only as a brief description of the methods employed, and for complete details, reference should be made to:

(1) "Standard Methods of Testing Petroleum and its Products, 2nd Edition," **1929** —Published by The Institution of Petroleum Technologists.
(2) "United States Government Master Specification for Lubricants and Liquid Fuels and Methods of Sampling and Testing," *U. S. Bureau of Mines Technical Paper* **323B**, 1927; and
(3) Index to "American Society for Testing Materials Standards and Tentative Standards," September, **1931**, American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa.

A distillation test for routine examinations must necessarily be simple and at the same time be capable of complete standardization in every detail likely to affect the results, so that substantial agreement may be obtained between different workers and different laboratories. The distillation tests of the A.S.T.M. and the I.P.T. meet these requirements. In each case, distillation is conducted in a small round-bottomed flask with side-arm, of definite dimensions, supported on an asbestos plate within a draught-proof cabinet. The condenser is a straight piece of brass tube resting in a cooling bath, and this, as well as every other part of the apparatus, is rigidly standardized.

The test, in the case of gasolines, naphthas and kerosenes, is carried out by distilling in the apparatus 100 ml. of material at a distillation rate of between 4 and 5 ml. per minute and recording either the volume of distillate obtained at temperatures that are even multiples of 25° C. (50°, 75°, 100° C., etc.) (I.P.T. procedure) or the temperatures registered on the thermometer when each successive 10 ml. of distillate is collected[145] (A.S.T.M. procedure). Observations of the temperature at which the first drop of liquid falls from the condenser tube, i.e., the "initial boiling point", the highest temperature recorded on the thermometer, i.e., the "end point", the amount of distillate collected in the receiver, i.e., the "recovery" or "total distillate" and the amount of undistilled residue, are also made. The difference between 100 ml. and the sum of the recovery and the "residue" is recorded as "distillation loss". With proper care and attention to the details prescribed, duplicate results obtained for initial boiling point and end point, respectively, should not differ from each other by more than 3° C. Duplicate readings of the volume of distillate collected in the receiver at different prescribed temperatures should not vary by more than 2 ml. The barometric pressure is also recorded, but no correction is applied except in cases of dispute, when the Sydney Young[146] equation is used.

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[139] *Bur. Standards J. Research,* 1930, **5**, 933; *Chem. Abs.,* 1931, **25**, 2275.

[140] Bruun and Hicks-Bruun, *Bur. Standards J. Research,* 1931, **7**, 607; *Chem. Abs.,* 1932, **26**, 286.

[141] Hicks-Bruun and Bruun, *Bur. Standards J. Research,* 1931, **7**, 799; *Chem. Abs.,* 1932, **26**, 1423.

[142] Washburn, Bruun and Hicks, *Bur. Standards J. Research,* 1929, **2**, 467; *Brit. Chem. Abs.* **B**, 1929, 345.

[143] Leslie and Schicktanz, *Bur. Standards J. Research,* 1931, **6**, 377; *Brit. Chem. Abs.* **B**, 1931, 660.

[144] Physical properties and their significance are also discussed in: Gruse, "Petroleum and Its Products," McGraw-Hill Book Co., Inc., New York, **1928**, 67; Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, **1932**, 180; Hicks-Cox, "Mineral Oil Testing," Charles Griffin and Co., Ltd., London, **1925**; Hamor and Padgett, "The Technical Examination of Crude Petroleum, Petroleum Products and Natural Gas," McGraw-Hill Book Co., Inc., New York, **1920**.

$$C = 0.00012\ (760 - P)\ (273 + t)$$

in which C = correction to be added (° C.) to the observed temperature (t); P = actual barometric pressure.

With gasoline, the asbestos plate supporting the distillation flasks has cut in it a circular hole, 1¼ inches in diameter, but when kerosenes are distilled, an asbestos plate with a 1½ inch hole is used. Similarly, the cooling bath is filled with ice when gasolines are distilled, but with water at a temperature not higher than 21° C. when kerosene or similar distillates are examined. According to I.P.T. methods, gas oils and Diesel oils are examined for distillation characteristics by distilling from a 500 ml. side-arm flask supported on a sand bath.

The distillation test is of especial importance in the examination of motor fuels because the boiling range of a gasoline and its content of volatile constituents have been shown to be intimately related to its general performance in an engine.[147]

Color Tests

Color tests are used to determine the extent of refining of gasolines, kerosenes and lubricating oils. Three kinds of instruments are used for this purpose: (1) The Lovibond Tintometer, which is specified in I.P.T. tests for gasolines, naphthas and paraffin waxes; (2) the Saybolt Chromometer, which is used in A.S.T.M. tests for gasolines, kerosenes and naphthas; and (3) the Union Colorimeter for standard A.S.T.M. lubricating oil tests. In each of these instruments a beam of white light is passed through a color glass and another is passed through the oil. The colors of both beams are compared. The color of the oil sample may then be matched with that of the standard glass either by varying the depth of the oil—as in the Saybolt Chromometer—or by changing the standard color glasses—as in the Union Colorimeter and the Lovibond Tintometer. A photoelectric colorimeter, which removes some of the difficulties in matching colors, has been described by Story and Kalichevsky.[148]

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[145] This procedure is sometimes varied in that the volume of distillate is recorded at temperatures which are even multiples of 10° (e.g., 40°, 50°, etc.). This permits an easy and rapid comparison of Centigrade and corresponding Fahrenheit temperatures.

[146] "Fractional Distillation," Macmillan and Co., Ltd., London, 1903, 14.

[147] Brown, Skinner, Bigby and Nickols, *Univ. Michigan, Eng. Res. Bulletin* 14, 1930; *Brit. Chem. Abs.* **B**, 1930, 934; *Ind. Eng. Chem.*, 1930, **22**, 278, 649, 653, 662. Edgar, Hill and Boyd, *Oil and Gas J.*, 1930, **29** (26), 144, 256, 259; *Chem. Abs.*, 1931, **25**, 406; Blair and Alden, *Ind. Eng. Chem.*, 1933, **25**, 559.

[148] *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 214.

TESTS FOR SULPHUR AND SULPHUR COMPOUNDS

Various sulphur compounds occur in motor fuels and other petroleum fractions, their type and proportion depending upon the source of the crude from which they are derived and the refining to which they have been subjected. In motor fuels and kerosenes, certain sulphur compounds must be removed, because of their offensive smell and corrosive action. Petroleum fractions intended for use as fuels must not contain more than a small amount of sulphur compounds because of the corrosive combustion products (principally sulphur dioxide) formed (see Chapter 19). Consequently, tests for sulphur compounds in petroleum distillates are performed in such a way as to differentiate between the offending sulphur bodies and those which can be tolerated. Thus, separate tests are employed for elemental sulphur, hydrogen sulphide, sulphur dioxide and mercaptans, the other sulphur compounds being classed as "residual" sulphur. The total sulphur content of fuels is generally limited to about 0.10 per cent as an extra precaution.

The I.P.T. method for testing for *elemental sulphur* in light oils makes use of the reaction between sulphur and mercury, with the addition of a small amount of dilute hydrochloric acid to the reaction mixture to coagulate the sulphide produced.[149] The precipitated sulphide is digested with hydrochloric acid, to which a small quantity of potassium chlorate is added, and subsequently diluted and filtered. The sulphur is precipitated as barium sulphate and estimated in the usual way. This method is, however, criticized by Hoffert[150] on the ground that loss of hydrogen sulphide, when the mercuric sulphide is dissolved in acid, produces low results with high sulphur concentrations.

Garner and Evans[151] described a method for estimating elemental sulphur in light oils by refluxing with copper-bronze powder. The bronze is then separated from oil by filtration and dissolved in bromine, together with the sulphide produced. A little hydrochloric acid is added and the excess bromine boiled off and the sulphur precipitated as barium sulphate in the usual way.

A modification of the Halphen[152] method of estimating cottonseed oil has been proposed by Thornton and Latta[153] for the colorimetric determination of free sulphur in petroleum distillates. The oil is treated with a mixture of 80 cc. of refined, unbleached cottonseed oil, 80 cc. of carbon disulphide and 8 cc. of pyridine at 100° C. for 30 minutes. The color developed is compared with standards.

Mercaptans are objectionable constituents of motor fuels and kerosenes because of their offensive odor and corrosive action. The common method of removing mercaptans in refining practice is with the so-called "doctor" solution. which consists of a solution of litharge (PbO) in caustic soda. The doctor test, which uses the same reagent, is the common method of test for mercaptans in light oils. The chemistry of the reaction has been discussed in Chapter 19.

The doctor test is briefly as follows: A small quantity of both the petroleum distillate and doctor solution are placed in a test tube and thoroughly agitated. The tube is then allowed to stand until the mixture has separated into two layers. A pinch of sulphur is next added to the oil (upper) layer, and the contents of the tube are again thoroughly agitated. The test tube is again allowed to stand to allow the mixture to separate into two layers. The appearance of black lead sulphide at the junction of the two layers indicates the presence of mercaptans in the distillate. If a large quantity of mercaptans is present, the distillate becomes yellow after shaking with the doctor solution as a result of the formation of soluble lead mercaptides. This also furnishes an indication of the presence of mercaptans. The doctor test for mercaptans is specified by both the A.S.T.M. and the I.P.T.

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[149] Ormandy and Craven, *J. Inst. Pet. Tech.*, 1923, 9, 133; *Chem. Abs.*, 1923, 17, 2772.

[150] 2nd Report of the National Benzol Association, Mar. 1925; *J.S.C.I.*, 1925, 536B; *Gas J.*, 1925, 170, 654; *Chem. Abs.*, 1926, 20, 1137.

[151] *J. Inst. Pet. Tech.*, 1931, 17, 451; *Chem. Abs.*, 1931, 25, 5278.

[152] *J. pharm. et chim.*, 1897, 6 (9), 390; *J.S.C.I.*, 1897, 16, 1045.

[153] *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 441.

If a black precipitate of lead sulphide is formed almost immediately when the distillate and the doctor solution come in contact before agitation, this is usually taken as an indication of the presence of hydrogen sulphide in the distillate.

2,4-Dinitrochlorobenzene has been suggested for the identification of mercaptans by Bost, Turner and Norton.[154] The mercaptans combine with this reagent, yielding solids that are easily purified and have sharp melting points and definite crystalline structure. The iodometric method for the estimation of mercaptans and its various modifications are mentioned in Chapter 19.

Various tests are used to indicate the presence of elemental sulphur, or of *corrosive sulphur compounds* in light oils.[155] Copper is generally the metal used for the manifestation of the corrosive action. In the well-known copper dish test, 100 ml. of light naphtha (e.g., aviation gasoline) are evaporated from a hemispherical copper dish placed upon a water bath. If the inside of the dish becomes colored or corroded the presence of objectionable sulphur compounds is indicated, whereas if the naphtha contains undesirable gum-forming constituents a weighable amount of gum is deposited on the dish.[156] In another method a strip of freshly polished copper is allowed to stand in the sample to be tested for 3 hours[157] at a temperature of 50° C. (122° F.).

Two general methods are employed for the *total sulphur determination:* one is the "lamp" method, applicable particularly to the determination of the sulphur content of lighter distillates such as gasoline or kerosene, and the other is the bomb calorimeter method, used with heavier oils.

In the lamp method a weighed quantity of the distillate is burned in a current of air and the products of combustion, together with the excess air, are passed through a dilute, standard solution of sodium carbonate.[158] Any sulphur compounds in the sample are burned to sulphur dioxide, which is absorbed by the carbonate solution with the formation of sodium sulphite. The oxygen present in the excess air in the combustion mixture oxidizes the sodium sulphite to sodium sulphate. Titration of the carbonate solution, with a standard solution of acid, before and after absorption, indicates the quantity of sulphur dioxide formed and from this can be calculated the quantity of sulphur in the oil.

If *chlorine* is present with the sulphur, it can be estimated, according to Wirth and Stross,[159] in a similar way. The gasoline is burned in a lamp in the usual way, the combustion products being absorbed in standard sodium carbonate solution. The excess sodium carbonate is then titrated with standard sulphuric acid, and the chlorine is subsequently titrated with silver nitrate solution by Mohr's method. The first titration gives the acidity due to the formation of hydrochloric and sulphuric acids. After the chlorine has been determined, the acidity resulting from the sulphuric acid alone can be calculated.

[154] *J.A.C.S.*, 1932. 54, 1985.

[155] Numerous tests for indicating corrosive sulphur compounds were investigated by Garner and Evans, *J. Inst. Pet. Tech.*, 1931, 17, 451.

[156] Methods for the determination of gum-forming constituents are described in Chapter 40.

[157] Sometimes 30 minutes at 100° C. (212° F.) is used instead of the longer period.

[158] An improved lamp for this combustion is described by Plonskier, *Ann. chim. analyt.*, 1932, (2) 14, 154; *Brit. Chem. Abs.* B, 1932, 968.

[159] *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 85.

In the bomb method the sample is burned in the presence of a large excess of oxygen. The sulphur is converted to sulphuric acid, and the quantity of acid produced can be determined in the usual manner by precipitating as barium sulphate and weighing. An adaptation of this bomb method has been described by Woodward.[160]

Electrolytic oxidation of the sulphur in mineral oils to sulphones, in the presence of nitric acid, has been described by Boisselet and Kryloff.[161]

A method of determining sulphur in oils by fusion with calcium hydride, which converts the sulphur to calcium sulphide, has been developed by Caldwell and Krauskopf.[162] The sulphide can be estimated by titration of the acidified solution of the fusion residue with iodine.

Sulphur may also be detected by boiling with metallic sodium and testing with sodium nitroprusside.[163] Grote[164] dissolved the compound to be tested in water and added an excess of sodium bicarbonate, followed by a reagent consisting of sodium nitroprusside, hydrazine hydrochloride and bromine. Characteristic colors were observed with various sulphur compounds.

OTHER METHODS FOR THE ESTIMATION OF SULPHUR COMPOUNDS

The amounts of the various general types of sulphur compounds in petroleum distillates can be estimated by the method of Faragher, Morrell and Monroe[165] which follows:

A small quantity of the oil is shaken with a slightly acidified solution of cadmium chloride. The percentage of *hydrogen sulphide* is calculated from the weight of cadmium sulphide precipitated. Caustic soda solution cannot be used in this test because it dissolves some of the mercaptans in addition to hydrogen sulphide.

According to Trusty,[166] hydrogen sulphide in natural gas can be determined by absorption in iodine solution. In refinery gases containing unsaturated hydrocarbons which react with iodine, the hydrogen sulphide can be precipitated as lead sulphide from lead nitrate solution, the excess of the latter being titrated with ammonium molybdate. Givaudin[167] removed hydrogen sulphide from petroleum with nitrogen and passed the resulting gas mixture into zinc acetate solution. The precipitated zinc sulphide was determined iodometrically.

After removal of sulphuretted hydrogen, *elemental sulphur* is estimated by the mercury treatment already described.

After removal of hydrogen sulphide and elemental sulphur, the *mercaptans* may be removed by treatment with alcoholic plumbite solution—an alcoholic solution being used to give better contact between the oil and the plumbite. Total sulphur estimation before and after this treatment gives the mercaptan sulphur content.[168]

[160] *Ind. Eng. Chem., Anal. Ed.*, 1929, 1, 117; *cf.* Nikaido, *J.A.C.S.*, 1902, 24, 774.

[161] *Compt. rend. Congr. Graissage*, 1931, 60; *Chem. Zentr.*, 1932, 2, 2575; *Brit. Chem. Abs.* **B**, 1933, 374.

[162] *J.A.C.S.*, 1930, 52, 3655.

[163] See Lomax, *Pet. Rev.*, 1917, 37, 251, 269; *Petroleum World*, 1917, 14, 477; *Chem. Abs.*, 1918, 12, 421.

[164] *J. Biol. Chem.*, 1931, 93, 25; *Brit. Chem. Abs.* **A**, 1931, 1268; Givaudin (*Rev. pétrolifère*, 1932, 892; *Chimie et industrie*, 1932, 29, 309; *Chem. Zentr.*, 1932, 2, 2270; *Chem. Abs.*, 1933, 27, 2791), describes the application of this test to sulphur in petroleum.

[165] *Ind. Eng. Chem.*, 1927, 19, 1281.

[166] *Refiner*, 1931, 10 (7), 91; *Brit. Chem. Abs.* **B**, 1932, 826.

[167] *Rev. pétrolifère*, 1932, 892; *Chimie et industrie*, 1932, 29, 309; *Chem. Zentr.*, 1932, 2, 2270; *Brit. Chem. Abs.* **B**, 1933, 180.

[168] An alternate method for the estimation of mercaptans consists in agitating the sample with an aqueous suspension of basic lead acetate, separating the oil and water layers, and determining the

Alkyl disulphides may be determined, after removal of mercaptans, by reducing them to mercaptans with glacial acetic acid and zinc dust. The resulting mercaptans may be estimated in the manner described above.

After the above successive treatments, the oil should contain no sulphur compounds other than alkyl sulphides and thiophenes. *Alkyl sulphides* can be estimated by treating the oil with an aqueous solution of mercurous nitrate—with which alkyl sulphides form addition compounds of the general type $R_2S.HgNO_3$. Total sulphur determinations before and after this treatment reveal the amounts of *alkyl sulphides* and *thiophenes* present. A method for the determination of alkyl sulphides in the absence of unsaturated hydrocarbons has been described by Sampey, Slagle and Reid.[169]

FLASH POINTS

The flash point of an oil may be defined as the temperature at which an oil evaporates so intensively that its vapor, in an open space of specified dimensions or in any other specified container, forms an ignitible mixture with air. This temperature must not be confused with the "burning point", that temperature at which the intensity of the evaporation is such that the vapors not only flash on the approach of a flame, but continue to burn. Both these values, particularly the first one, are of aid in indicating fire risks. The lower the flash point of an oil, the more likely is it to evaporate and form an explosive vapor, and consequently greater precautions against fire in storage and distribution are necessary.

For the determination of the flash points of petroleum oils, many types of apparatus are used, depending upon the kind of oil to be tested. The better-known are: (1) the Abel apparatus used in the I.P.T. standard tests for kerosenes and all oils having a flash point below 90° F. (32.2° C.); (2) the Pensky-Mortens apparatus used in I.P.T. standard tests for all oils having a flash point of above 90° F.; and (3) the Cleveland open cup tester which is used in the testing of heavy oils. Each of these types are similar in mode of operation. The oil to be tested is heated in a small container at a specified rate and at certain intervals of temperature a small test flame is applied to the vapor space above the liquid. The lowest temperature at which the oil vapor or mixture gives a momentary flash is taken as the flash point. Further details concerning the determination of flash points are given in the standard publications mentioned at the end of this chapter.

VISCOSITIES OF PETROLEUM OILS

As in the case of flash points, the viscosities of petroleum oils are usually measured in an apparatus specially designed for this purpose. Arbitrary scales of viscosity units have been in general use in the petroleum industry ever since its inception. Measurements are usually made, as in the well-known Redwood, Saybolt, and Furol viscometers, by determining the rate of efflux of oils through calibrated orifices under rigidly specified conditions. The time taken for the efflux of a specified volume of oil is usually taken as the index of viscosity. Thus, when the viscosity of an oil is given as 50 seconds Saybolt at some tem-

quantity of sulphuric acid required to react with the mercaptides. The equations given for the reactions taking place are:

$$Pb(OH)(C_2H_3O_2) + 2RSH \rightarrow (RS)_2Pb + HC_2H_3O_2 + H_2O$$
$$Pb(SR)_2 + H_2SO_4 \rightarrow PbSO_4 + 2RSH$$

Borgstrom and Reid (*Ind. Eng. Chem., Anal. Ed.,* 1929, 1, 186) suggested agitating the sample with a given volume of standard silver nitrate solution, removing excess silver nitrate with standard ammonium thiocyanate solution, and titrating excess thiocyanate with standard silver nitrate solution.

[169] *J.A.C.S.,* 1932, 54, 3401.

perature, it means that it has an efflux time of 50 seconds at that temperature from a Saybolt viscometer. Further details concerning these measurements are given in the standard publications of the Institution of Petroleum Technologists and The American Society for Testing Materials. Convenient methods for the determination of the viscosities of oils in absolute units are described by The British Engineering Standards Association in their Specification No. 188 (1929).

OTHER TESTS USED IN THE EXAMINATION OF PETROLEUM PRODUCTS

Other tests used by the petroleum industry in the examination of mineral oils include burning tests for kerosene, tests for acidity and alkalinity, determination of calorific values (i.e., heats of combustion), ash contents, and oxidation tests for lubricating oils.[170] Most of these tests are outside the scope of the present volume and the reader is referred to the previously mentioned publications for further particulars. Other references which may be consulted are:

(1) Holde, "Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes"—translated from the German by Mueller, John Wiley and Sons, New York, 1918.
(2) Specifications for Petroleum Products drawn up by the United States Government (Government Printing Office).
(3) Specifications for Petroleum Products used by English Government Departments (H.M. Stationery Office).

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[170] Gum tests are described in Chapter 40.

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